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# A HANDBOOK

OF

# INORGANIC CHEMISTRY.

For the Use of Students.

BY

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FOURTH EDITION,

CORRECTED AND ENLARGED.

264698  
17.2.32

LONDON:

WALTON & MABERLY,

UPPER GOWER STREET, AND IVY LANE, PATERNOSTER ROW.

1857.

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LONDON:  
FRADBURY AND EVANS, PRINTERS, WHITEFRIARS.

## PREFACE TO THE FOURTH EDITION.

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IN preparing this Fourth Edition of my Handbook of Inorganic Chemistry, I have endeavoured to make such alterations and additions as have been rendered necessary by the progress of this branch of the science ; and it will be found that but few sections are without considerable additions, which I trust will be deemed improvements.

But while this is the case, I have been particularly careful not to change the character of the work, as it appeared in the Third Edition, which seemed, to judge by the favourable reception it has met with, to have supplied a want that had been felt ; the want, namely, of a work of moderate size, which might be placed in the hands of beginners, and which, while strictly scientific in its character, should be neither too voluminous nor too technical for the greatly increased number of persons who, without the intention of becoming practical chemists, yet desire to have an accurate notion of the fundamental principles of Chemistry, as well as of the more important facts of that science, and their bearing on the useful arts.

I have great hopes that this work may prove a useful guide to teachers, and that to students it may serve as a safe introduction to the study of Chemistry, whether they

intend to pursue it practically or not. In the former case, other and more special works must follow.

I take this opportunity of acknowledging, with gratitude, the very favourable reception which has been accorded to the previous editions; and of expressing the hope that the present one may be found to answer the purpose for which it has been prepared.

WILLIAM GREGORY.

UNIVERSITY OF EDINBURGH,  
*September, 1857.*

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# ERRATA.

Page 110, line 23, for "trimethylamine" read trimethylamine.

„ 226, „ 17, for " $\text{Li O} = 14.5$ " read  $\text{Li O} = 14.95$ .

„ 230, „ 12, for "insoluble with lead" read insoluble: with lead.



# INORGANIC CHEMISTRY.

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## INTRODUCTORY.

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THE world in which we live is formed, in its different parts, of a number of distinct kinds of matter, amounting according to the present state of our knowledge, to about 62. These are called elements, elementary bodies, or simple substances.

The forms of matter with which we are most familiar, however, are not elementary. If we examine the matter of which a rock, a tree, an animal, the atmosphere, and the ocean are respectively composed, we shall find that all those objects may be proved to contain two or more distinct kinds of matter ; that is, two or more elements. Where this is the case, we call the substance a compound body.

A compound, therefore, may be resolved into its elements ; whereas an element, or simple substance, cannot be made by any means yet known to us, to yield more than one kind of matter. Brass, which is compound, may be resolved into copper and zinc ; but from copper or zinc we can obtain only copper or zinc. Vermilion may be shown to contain sulphur and mercury ; but sulphur can only be made to yield sulphur, and mercury, mercury.

But when we call any substance elementary, or simple, we do not mean that it is certainly or essentially so ; we only say that hitherto, in our hands, and exposed to all the various agencies which we can bring to bear on it, it has yielded only one kind of matter, or element, and no more. In the early part of the present century, the alkalies and earths were believed to be elementary bodies, because only one kind of matter had ever been obtained from them : but the new power of galvanism enabled Davy to discover that all these bodies were compound.

It is far from being improbable, that in the progress of discovery, several, perhaps many, of the 62 elements which we are now compelled to admit, may, in like manner, prove to be really compound bodies.

Till then, however, we must be content to class together, as elements, all those bodies which have not yet been resolved into other kinds of matter ; and of these undecomposed bodies, or elements, all material objects are constituted. Here follows the list of the elementary bodies at present admitted, with the abbreviation or symbol which is used for each element, placed after the name :—

## ELEMENTS.

|                              |    |                                 |    |
|------------------------------|----|---------------------------------|----|
| Oxygen . . . . .             | O  | Manganese . . . . .             | Mn |
| Hydrogen . . . . .           | H  | Iron (Ferrum) . . . . .         | Fe |
| Nitrogen . . . . .           | N  | Cobalt . . . . .                | Co |
| Sulphur . . . . .            | S  | Nickel . . . . .                | Ni |
| Phosphorus . . . . .         | P  | Zinc . . . . .                  | Zn |
| Carbon . . . . .             | C  | Cadmium . . . . .               | Cd |
| Chlorine . . . . .           | Cl | Lead (Plumbum) . . . . .        | Pb |
| Bromine . . . . .            | Br | Tin (Stannum) . . . . .         | Sn |
| Iodine . . . . .             | I  | Bismuth . . . . .               | Bi |
| Fluorine . . . . .           | F  | Copper (Cuprum) . . . . .       | Cu |
| Boron . . . . .              | B  | Uranium . . . . .               | U  |
| Silicon . . . . .            | Si | Mercury (Hydrargyrum) . . . . . | Hg |
| Selenium . . . . .           | Se | Silver (Argentum) . . . . .     | Ag |
| Potassium (Kalium) . . . . . | K  | Palladium . . . . .             | Pd |
| Sodium (Natrium) . . . . .   | Na | Rhodium . . . . .               | R  |
| Lithium . . . . .            | L  | Ruthenium (?) . . . . .         | Ru |
| Barium . . . . .             | Ba | Iridium . . . . .               | Ir |
| Strontium . . . . .          | Sr | Platinum . . . . .              | Pt |
| Calcium . . . . .            | Ca | Gold (Aurum) . . . . .          | Au |
| Magnesium . . . . .          | Mg | Osmium . . . . .                | Os |
| Aluminium . . . . .          | Al | Titanium . . . . .              | Ti |
| Glucinum . . . . .           | G  | Columbium (Tantalum) . . . . .  | Ta |
| Yttrium . . . . .            | Y  | Pelopium . . . . .              | Pe |
| Zirconium . . . . .          | Z  | Niobium . . . . .               | Nb |
| Thorium . . . . .            | Th | Norium (?) . . . . .            | No |
| Cerium . . . . .             | Ce | Tellurium . . . . .             | Te |
| Lanthanum . . . . .          | La | Tungsten (Wolfram) . . . . .    | W  |
| Didymium . . . . .           | D  | Molybdenum . . . . .            | Mo |
| Erbium . . . . .             | E  | Vanadium . . . . .              | V  |
| Terbium . . . . .            | Tb | Chromium . . . . .              | Cr |
|                              |    | Antimony (Stibium) . . . . .    | Sb |
|                              |    | Arsenic . . . . .               | As |

The symbols or abbreviations are in every case taken from the Latin names of the elements, so as to be universally understood.

Of the above list of elements, about 14 constitute the great mass of our earth and of its atmosphere. These are Oxygen, Hydrogen, Nitrogen, Chlorine, Sulphur, Phosphorus, Carbon, Silicon, Potassium, Sodium, Calcium, Magnesium, Aluminium

Iron. It is remarkable that the same elements which constitute the solid earth, the waters, and the air, are also, with the exception of aluminium, the elements of plants and of animals. This, as will be more fully explained in the Organic Chemistry, enables us to understand how it comes to pass, that the food of plants is exclusively mineral or inorganic in its forms, while plants constitute the food of animals ; and the products, both of animal life, and of the putrefaction and decay of dead animals and plants, ultimately resume those mineral forms which alone can support the life of a new generation of vegetables. Thus a large portion of the above-named elements, excepting aluminium, are constantly passing through an endless circle of transformations, in which plants and animals are mutually dependent, while both depend on the mineral world.

The remaining elements occur scattered, and, comparatively, in small quantity. Many of them are, as it were, concentrated by nature in certain spots, as the metals generally are in what are called metallic veins ; and are thus rendered available to man, when they possess useful properties. But nearly a third of the whole number of elements are either not known to have useful properties, or are so rare as not to admit, practically, of any useful application.

By their external aspect, the elements may be divided into two classes ; and these classes are also found to possess other distinctive characters. Thus the thirteen first in the list, which are called non-metallic bodies, or metalloids, are easily distinguished from all those after potassium, inclusive, which are metals. The latter possess that peculiar brightness and opacity of surface which is called the metallic lustre, of which the former are destitute. Again, the metals are all found to be excellent conductors of heat and electricity, while the metalloids conduct these influences very badly, with the exception of carbon, which, when in certain states, conducts electricity almost like a metal.

Selenium has the metallic lustre, and is by some considered a metal ; but it is a non-conductor of heat and electricity, and in all its chemical relations and analogies belongs to the non-metallic bodies.

This division of the elements is of great use in facilitating the study of chemistry.

The elements are capable of combining together, metalloids with metalloids, metals with metals, and metalloids with metals.

When two elements unite together, they give rise to a new substance, a compound of the two ; and, generally speaking, the compound has properties entirely distinct from those of its

elements. Thus, sulphur and mercury, a yellow earthy solid and a white fluid metal, unite, and give rise to a fine red powder which is vermilion. It is not possible, by the eye, to distinguish two kinds of matter in the vermilion, any more than in its elements, so completely have the properties of those elements disappeared. But, by chemical means, we can prove that vermilion contains both mercury and sulphur. These elements are said to be combined, so as to produce vermilion, which is said to be a compound, or to be composed of them. In such a case, the combined elements can no longer be separated mechanically from each other. They are held together by a force which is called chemical attraction, or *affinity*, the real nature of which we do not know. It resembles cohesion, since it holds together the particles of matter : but while cohesion is only exerted between particles of the same nature, as, for example, between those of sulphur, or between those of vermilion, affinity is only exerted between particles of different kinds of matter, for example, between the particles of sulphur and of mercury.

By affinity, then, we understand simply that force, whatever may be its nature, by which the particles of one elementary body are made to unite with those of another. When once united, the particles of the compound obey the laws of cohesion exactly as if they were simple particles.

It is the object of chemistry to investigate the properties of the elements, the laws which regulate their mutual actions, and the nature and properties of the compounds which arise from their union.

Before describing the individual elements, it is necessary to explain to the reader certain terms and phrases of very frequent occurrence, as well as to mention the general laws which regulate chemical combination.

*Combination* occurs when two or more bodies unite together : *decomposition* takes place when bodies, previously united, are made to separate from each other.

When oxygen enters into combination with any other element, the compound is called an oxide ; the compound of chlorine with any other element is called a chloride : and with bromine, iodine, and fluorine, we have, in the same way, bromides, iodides, and fluorides. The compounds of sulphur, phosphorus, carbon, selenium, &c., with metals, are called sulphurets, phosphurets, carburets, seleniurets, or sulphides, phosphides, carbides, selenides, &c. The latter form is gradually coming into general use ; but both are still employed.

When a compound body possesses a sour taste, reddens vegetable blue colours, and neutralises alkalies, it is called an acid

If composed of oxygen united to a metalloid, such as carbon, or a metal, such as chromium, the acid is simply named from the metalloid or metal, as carbonic acid, chromic acid. But if the acid contains hydrogen united to a metalloid, the word "hydro" is prefixed; as hydro-chloric acid (hydrogen and chlorine), hydro-sulphuric acid (hydrogen and sulphur), &c. Many continental chemists prefer the terms "chlorhydric" to "hydro-chloric," and "sulphhydric" to "hydrosulphuric." These are awkward terms in English, but have the advantage of avoiding the ambiguity which might attach to the prefix "hydro," which has sometimes been used to indicate the presence of water in a compound. We shall continue the use of "hydrochloric," &c., but avoid the use of "hydro" to indicate the presence of water, employing instead of it, the terms "hydrate of" or "hydrated," according to circumstances.

Where the same element forms with oxygen several acids, they are distinguished by their terminations, as sulphuric acid, sulphurous acid: the acid in *ic* always containing most oxygen: but where new acids of intermediate composition are discovered, it is necessary to use the prefix "hypo,"—as hypo-sulphurous acid, hypo-sulphuric acid, meaning acids containing less oxygen than sulphurous or sulphuric acids respectively; or "hyper," as hyper-chloric acid, meaning an acid containing more oxygen than chloric acid. The prefix "hyper" is often abbreviated to "per;" thus, perchloric and permanganic acids are the same as hyperchloric or hypermanganic acids.

When a compound body has an acrid, urinous taste, restores to blue the colour reddened by an acid, and above all, if it possess the property of neutralising acids, or causing their acid properties to disappear, it is called an alkali, or more generally a base, or a basic substance.

It may happen that either an acid or a base may be sparingly soluble, or even insoluble in water; in which case the one cannot exhibit the sour, nor the other the alkaline taste; they may thus also be incapable of acting directly on vegetable colours. Thus silicic, stannic, tungstic, and antimonie acids, and the bases magnesia, oxide of zinc, and oxide of lead, are insoluble, or nearly so. In such cases, the acid or basic character is recognised by the power of the acids to unite with and neutralise bases, and by that of the bases to unite with and neutralise acids.

We have seen that oxygen is an element of many acids; it is also an element in most bases. Almost all the metals are capable of forming one base, several form more than one base, with oxygen. These bases are usually called oxides of the

metal ; and where there are two, that which contains least oxygen is usually called protoxide, and that which contains most oxygen, peroxide ; as the protoxide and peroxide of iron, &c. Where there are several oxides, they are often named by means of the Greek numerals ; thus, we have the protoxide, deutoxide, tritoxide, and tessaroxide of osmium, in which one equivalent of the metal is combined with 1, 2, 3, and 4 equivalents of oxygen ; and pentasulphide of potassium contains five equivalents of sulphur to one of potassium.

Acids and bases unite together, and the characteristic properties of both disappear. They are said mutually to neutralise each other, and the resulting compound is called a salt. If neither the acid nor base be in excess, the salt is a neutral salt ; if the acid predominate, it is called an acid salt, or a super-salt, and if the base prevail, it is called a basic salt, or a sub-salt. The salt is named from both the ingredients. Thus, when sulphuric acid neutralises soda, the resulting salt is called the sulphate of soda ; when phosphoric acid unites with lime, the acid being in excess, the salt is called acid phosphate of lime, or superphosphate of lime ; and when nitric acid unites with oxide of mercury, the latter being in excess, the compound is called basic nitrate of mercury, or subnitrate of mercury. Salts with excess of acid are also named by means of Roman numerals prefixed ; thus we have bisulphate of potash, tersulphate of alumina, quadroxalate of potash, according as the equivalents of acid are 2, 3, or 4. When the base is in excess, Greek numerals are prefixed according to the number of equivalents of base ; as dinitrate of mercury, triacetate of lead, &c.

Besides acids and bases, there is a third kind of oxides, namely, such as have neither acid nor basic properties. They are called indifferent oxides, and sometimes superoxides ; as for example, peroxide, properly superoxide of manganese, deutoxide or superoxide of lead, and water. Water, however, though a neutral or indifferent body in many circumstances, is capable, as we shall see, of playing the part either of a weak acid or of a weak base, when it combines with bases or acids respectively.

The term “radical” is applied to any body which, by uniting with an element, can give rise to an acid or a salt. Most of the elements play the part of radicals : but we have besides compound radicals, containing two elements, like cyanogen, or even three or more elements, like benzoyle or kakodyle. The compound radicals unite with elements, just as if they were themselves elementary. Thus, cyanogen unites with hydrogen to form an acid, and kakodyle unites with oxygen to form a base.

## COMBINATION.

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THE force of chemical attraction, or affinity, is unequal in the case of different substances. Thus, the affinity between potassium and oxygen is more powerful than that between gold and oxygen.

The capacity of one body to unite with another is mainly affected by two circumstances ; namely, the state or form of the substances in question, whether solid, liquid, or gaseous, and the temperature at which they are brought together.

Cohesion tends to keep the particles of bodies in close proximity, while the tendency of heat is to separate them from each other. When cohesion predominates over the repulsion due to heat, the body is solid : when cohesion and repulsion are exactly balanced, it is liquid ; and when repulsion predominates, it becomes gaseous.

It is obvious that, since chemical attraction operates between the particles of different bodies, and only when they are at infinitely small distances, the cohesion between the particles of two solid bodies respectively must impede chemical action by preventing the sufficiently close approximation and intermixture of the particles which have affinity for each other. Hence the solid form is most unfavourable to chemical action, although, in rare cases, the power of affinity is sufficient to overcome the obstacle. Thus, phosphorus and iodine, both in the solid form, act powerfully on one another.

But if one or both of the bodies be liquid, the particles of both readily come so near as to admit of affinity producing its full effect. Thus, bromine acts violently on phosphorus, although the latter is solid ; nitric acid, in like manner, dissolves metals, and the same acid acts with great energy on alcohol, and on oily substances. Indeed, the liquid form is so favourable to chemical action, that the chemist generally endeavors to have one or both of the substances, whose action he wishes to try, in that form.

Moreover, when two solid bodies, as is generally the case,

refuse to act on each other, it is commonly sufficient to cause one of them to assume the liquid form. This may be done in two ways ; either by applying a sufficient heat to melt it, or by dissolving it in water or some other solvent. Thus iron and sulphur, when mixed in the solid form, do not combine ; but if the sulphur be melted by heat, and the temperature raised to about the boiling point of sulphur, rapid combination takes place. Again : citric acid and carbonate of soda do not act on each other when dry ; but if water be added to the mixture, the acid dissolves, and brisk action ensues.

It is evident that heat, being opposed to cohesion, will promote chemical action whenever cohesion or the solid form is the obstacle : and this is the source of the immense value of heat in chemical and manufacturing processes ; as, for example, in the smelting of metals from their ores.

But when cohesion has been still further overcome, and the body has assumed the gaseous form, a new impediment is offered to chemical action. The particles, by the predominance of the repulsion due to heat, are now so far removed from each other, as not to come readily within the sphere of chemical affinity. Hence, two bodies in the gaseous form seldom act on one another, unless their mutual attraction be very strong, as in the case of hydrochloric acid gas and ammoniacal gas ; or by the aid of heat, light, or electricity, as in the case of chlorine and hydrogen gases. As heat is here the cause of the obstacle, the appropriate remedies would seem to be cold and compression, which tend to bring the particles nearer. Yet the heat of a flame, and the electric spark, often produce the combination of two gases, as has just been mentioned. Heat is supposed, by some, to act by expanding the particles nearest to it, which in turn compress those farther off so as to bring them sufficiently near for affinity to act. The electric spark may also produce this effect, in virtue of its heat. But there can be no doubt that heat also, and perhaps chiefly, acts by exalting the intensity of chemical attraction or affinity.

Even where only one of the bodies is gaseous, chemical action is much impeded, especially if the other be solid. Still, in many cases, solids and liquids do slowly act on gases ; and by such means some of the most important processes in the organic kingdoms are carried on : as, for example, the respiration of animals, and the growth and decay of plants.

In some cases, as in that of hydrochloric acid gas, the affinity between the gas and water is so powerful, that they combine instantaneously when brought into contact.

There are other cases in which solid bodies at the ordinary



temperature are incapable of combining with gases, but in which a high temperature, although it opposes chemical action by its tendency to remove still further the particles of the gas, yet, on the other hand, so much exalts the power of affinity as to be the most powerful promoter of combination. The effect of heat in causing wood, coal, or charcoal, to combine with oxygen, as in ordinary combustion, is a familiar example of this : and as, in this form of experiment, the combustion, once begun, produces a great amount of heat without external aid, so that the combustion spreads from one particle to the next, in consequence of the high temperature, it is in this manner that heat is obtained and rendered available for the useful purposes above alluded to.

A gaseous body, which under ordinary circumstances will not combine with another substance, may be made to do so, if presented to it when the latter is also in the nascent state, that is, while it is separating from another solid or liquid body. Thus hydrogen gas, if formed in contact with sulphur, will not combine with it ; but if the hydrogen be formed by the action of an acid on sulphuret of iron, the sulphur is presented to the gas at the very moment at which the former is separating from the iron (in the nascent state, as it is called), and the gas which is now disengaged is a compound of sulphur and of hydrogen.

It sometimes happens that the combination of two bodies is promoted by the presence of a third, which does not combine with either of the two, nor even with the resulting compound. Thus, if oxygen and hydrogen gases be mixed, they do not combine ; but the contact of spongy platinum causes their immediate union, although the metal combines neither with oxygen nor with hydrogen, nor with water, the product of their combination.

But in all cases where the third body has a powerful affinity for the resulting compound, its effect in promoting combination is very great, and has got the name of predisposing affinity. Thus, zinc does not decompose water ; but if sulphuric acid be added, the water is decomposed, its oxygen uniting with the zinc. In this case, according to the usual explanation, the oxide of zinc formed unites with the acid, and the affinity of the acid for the oxide of zinc is called a predisposing affinity, as if the acid had caused the formation of oxide of zinc because of its affinity for that oxide when formed, as if the acid exerted an attraction for the oxide before the latter was formed, which is manifestly impossible. The truth is simply, that zinc alone is unable to separate oxygen from hydrogen ; but when sulphuric

acid is added, several affinities or attractions come into play. The chief of these is, the tendency of sulphur, zinc, and oxygen to form sulphate of zinc, which is opposed by the attraction between oxygen and hydrogen, the latter tending to keep matters as they are. But the former is assisted by the strong tendency of hydrogen to assume the gaseous form, and the result is that sulphate of zinc is formed and hydrogen set free. But all the changes that occur are strictly simultaneous, and the phrase "predisposing affinity" is not an accurate one. It is, however, sufficiently convenient and expressive to be a good deal used in regard to similar cases.

When two bodies, A and B, are in combination, the force with which they are actually held together is not dependent alone on their mutual affinity, but also on their relative mass. In the compound ABB, A is retained by a greater force than in AB. This is the result of the increased mass of B. Or we may view it thus:—In the compound AAB, the first A may be moved with comparative facility, the relative masses of A and B being equal. But after the removal of the first A, the mass of B is relatively doubled, and the second A requires for its removal a much greater force. It is obvious that, conversely, in ABB, the second B is less forcibly retained than the B in AB.

When a body, A, is presented to two bodies, B and C, for each of which it has affinity, although unequal, then, if nothing interfere, A will divide itself between B and C, according to its affinity for each. But the effect of mass is seen here also; for if the mass of C, the body for which A has least affinity, be much larger than that of B, then the division will be no longer in the ratio of the affinities to A, but C will obtain more, and B less, of A, than if relative affinities only had come into play.

When to a compound body, AB, another body, C, is added, having an affinity for B, both combination and decomposition occur: for AB is decomposed, and at the same time B, which separates from A enters into combination with C. It does not often happen that the mere force of affinity is sufficient to complete such a change, but such cases do occur: as when iron acts on a salt of copper, or copper on a salt of silver, the one metal taking the place of the other, and the latter being entirely separated. More frequently a part only of B is separated from A and combines with C; and thus there are present, at the same time, the compounds AB and BC, while a part of A and of C exists in the free or uncombined state along with them.

If now the free A be removed from the mixture, the free C

being unresisted, at last effects a complete separation of A. The removal of the free A is effected either when that body assumes the solid form by virtue of its great cohesion, or when it takes the form of gas in consequence of its feeble cohesive power, or of the application of heat. The precipitation of an insoluble oxide by a soluble alkali, and that of one metal from its solution by another are examples of the former ; the decomposition of water by potassium, when hydrogen is liberated, and the formation of glass by the fusion of silicic acid with carbonate of potash are illustrations of the latter case. Similar cases are of constant occurrence.

In both cases, the decomposition is the more easy and complete, the larger the mass of the decomposing body C employed. And from this follows the curious fact, that if, at any given temperature, we can alter the form or the mass of either of the bodies which act on one another, the result of the experiment is likewise altered : nay, it may actually be reversed. Thus, if oxide of iron be exposed at a red-heat to a current of hydrogen gas, the oxide is decomposed, its oxygen, with the hydrogen, forming water, while the iron is reduced to the metallic state. But if now the iron be heated red hot, and exposed to a current of the vapour of water, the water is decomposed, its oxygen, with the iron, forming oxide of iron ; while the hydrogen is reduced to the free state. In the first case, the current removes the oxygen from the field of action as fast as it is converted into water, while an excess of hydrogen is always presented to the undecomposed oxide. In the second, the hydrogen is removed as fast as liberated, so that an excess of oxygen is always presented to the metal. It is possible, however, that these opposite changes do not take place precisely at the same temperature, though the difference cannot be great. But we know that mercury when heated very nearly to its boiling point combines with the oxygen of the air ; and that, if the temperature be raised to the boiling point of the metal, or perhaps a little above it, the oxide just formed is decomposed, and the oxygen set free.

Decomposition is rendered complete, not only when the body A, which is separated, assumes the solid form, but also when A remains liquid or dissolved, and the new body, BC, takes the solid form, or is insoluble. Hence the nature of the liquid, in which a chemical action goes on, exerts a most important influence on the result of the action.

When two compound bodies, AB and CD, act on one another, both decomposition and combination occur. When complete, the change is called double decomposition, since both AB and

CD are decomposed ; but at the same time the two new combinations, AD and CB, have been formed. Should the change be only partial, the four compounds AB, CD, AD and CB, will be present together. Double decomposition is of very frequent occurrence.

In cases where a compound, AB, cannot be decomposed by a body, C, even with the aid of a high temperature, the addition of a fourth body, D, if it have an affinity for A, while there is an affinity between C and B, will often enable us to accomplish the decomposition. Thus oxide of aluminium cannot be decomposed by charcoal even at a white heat : but when a current of chlorine gas is passed over the mixture, the chlorine, by virtue of its affinity for aluminium, added to that of carbon for oxygen, effects the decomposition, and we obtain chloride of aluminium and oxide of carbon.

When a compound of three or more elements is exposed to a high temperature, the elements unite to form such new compounds as are not decomposable by the temperature employed.

If such a compound be heated along with a body which is capable of forming with some of the elements in certain proportions a more fixed compound, the remaining elements give rise to one or more, new and more volatile compounds.

The two last are the principal laws which regulate the phenomena of the destructive distillation of organic substances. But as oxygen is invariably an ingredient of organised substances, in rather small proportion, with a large amount of carbon and hydrogen, and generally some nitrogen, another principle comes into play. In virtue of their powerful attraction for oxygen, the carbon and hydrogen combine with that element, either together, if the temperature be moderately high, producing ternary compounds, such as acetic acid, pyroxylic spirit, creosote, &c., along with much water ; or, at a higher temperature, forming water and carbonic oxide. And as the oxygen present is soon consumed, compounds of carbon and hydrogen appear, especially towards the latter part of the operation, when the heat is strong. Thus we obtain gaseous carbo-hydrogens, such as coal gas or oil gas ; liquid carbo-hydrogens, such as naphthas and paraffine oils ; and, lastly, solid carbo-hydrogens, such as paraffines and naphthaline. Such are the chief products of the distillation, for example, of wood or of oil, where nitrogen is absent. When that element is present, there is formed in addition a numerous series of ternary compounds of carbon, hydrogen, and nitrogen, which are volatile basic oils, of very curious properties. Cyanogen, a compound of carbon and nitrogen, is only formed, at least

abundantly, when a base, such as potash, is added to the organic matter to be heated ; and it is found in the residue as cyanide of potassium.

Such are the most important facts in regard to the circumstances under which combination and decomposition occur. We now come to the subject of the proportions in which bodies combine together, or

## COMBINATION IN DEFINITE PROPORTIONS.

The experience of chemists, derived from many thousand analyses, has established the following laws ; which, however, are purely the expression of ascertained facts, and involve no hypothesis whatever :

1. The quantity, by weight, of the body B, which is taken up by a given weight of the body A, to produce the compound AB, is definite and unchangeable. Thus 8 grains of oxygen are invariably taken up by 1 grain of hydrogen to produce water : or, in other words, 9 grains of water are invariably composed of 8 grains of oxygen and 1 of hydrogen.

2. When a body A combines with a body B in more proportions than one, producing more than one distinct compound, the quantity, by weight, of B, which is united to the same weight of A in the different compounds, increases according to one of two ratios. According to one, the series of compounds formed is—

|            |              |   |   |   |       |
|------------|--------------|---|---|---|-------|
| A + B,     | 1st compound | . | . | . | B = 1 |
| A + BB,    | 2nd do.      | . | . | . | B = 2 |
| A + BBB,   | 3rd do.      | . | . | . | B = 3 |
| A + BBBB,  | 4th do.      | . | . | . | B = 4 |
| A + BBBBB, | 5th do.      | . | . | . | B = 5 |

According to the other, the series of compounds is—

|             |              |   |   |               |
|-------------|--------------|---|---|---------------|
| A + BBB,    | 1st compound | . | . | A : B = 1 : 3 |
| A + BBBBB,  | 2nd do.      | . | . | A : B = 1 : 5 |
| A + BBBBBB, | 3rd do.      | . | . | A : B = 1 : 7 |

The compounds of nitrogen and oxygen offer an example of the first series of multiple proportions. In the first of these compounds,

|             |    |                  |                 |              |
|-------------|----|------------------|-----------------|--------------|
|             | 14 | grs. of nitrogen | are united with | 8 of oxygen. |
| In the 2nd. | 14 | "                | "               | 16           |
| " 3rd.      | 14 | "                | "               | 24           |
| " 4th.      | 14 | "                | "               | 32           |
| " 5th.      | 14 | "                | "               | 40           |

The compounds of arsenic and oxygen will illustrate the second series. In the first of these compounds,

75 grs. of arsenic are united with 24 of oxygen.

|             |    |    |    |    |    |    |
|-------------|----|----|----|----|----|----|
| In the 2nd. | 75 | ,, | ,, | ,, | 40 | ,, |
|-------------|----|----|----|----|----|----|

Here the quantities of oxygen increase in the ratio of 3 to 5.

In some cases, there is a modified series, which is somewhat peculiar. After a compound in the proportion of 1 to 1, comes another in that of 2 to 3; this is followed by a third, and sometimes by a fourth, belonging to the first series, namely, 1 to 2 or 1 to 3; and lastly we find a compound exhibiting the ratio of 2 to 5, or even 2 to 7.

The compounds of manganese and oxygen illustrate this. We have, in the first of these compounds :—

|             |      |                                    |    |    |    |  |
|-------------|------|------------------------------------|----|----|----|--|
|             |      | 27·6 of manganese and 8 of oxygen. |    |    |    |  |
| In the 2nd. | 55·2 | ,,                                 | ,, | 24 | ,, |  |
| ,, 3rd.     | 27·6 | ,,                                 | "  | 16 | ,, |  |
| ,, 4th.     | 27·6 | ,,                                 | ,, | 24 | ,, |  |
| ,, 5th.     | 55·2 | ,,                                 | ,, | 56 | ,, |  |

The compounds of iron and of chromium also exhibit parts of this series. These compounds which have the proportion of 2 to 3, and which are not unfrequent, are called *sesqui-compounds*, because the ratio of 2 to 3 is the same as that of 1 to  $1\frac{1}{2}$ . Thus we have the sesquioxides of iron, manganese, chromium, and aluminium.

3. The proportions, by weight, in which bodies combine, are proportional to each other. That is : if a given weight of A unite with weights of B and C, which are to each other as 3 to 4, for example; then if a fourth body, D, unite with B and with C likewise, the weights of B and C combined with D will also be to each other as 3 to 4.

Thus, 100 grs. of potassium unite with 20·4 grs. of oxygen : 100 grs. of potassium unite also with 40·8 grs. of sulphur. Now 100 grs. of silver unite with 7·4 grs. of oxygen, and also with 14·8 grs. of sulphur. According to this law, we find that  $7·4 : 14·8 :: 20·4 : 40·8$ ; or, in other words, that the weights of oxygen and sulphur which unite with 100 grs. of silver bear to each other the same proportion as the weights of those elements which combine with 100 grs. of potassium.

Another consequence of this law is, that the weights of two bodies which combine with the same weight of a third body, will also represent the weights of these two bodies which unite together, if they are capable of combination; or if the proportions should not be precisely the same, they will be found to be multiples or submultiples of those weights.

Thus, 8 grs. of oxygen combine with 1 grain of hydrogen to form water ; and 8 grs. of oxygen combine with 16 of sulphur to form hyposulphurous acid. Now, sulphur and hydrogen combine together to form hydrosulphuric acid ; and that compound is found to contain sulphur and hydrogen in the proportion of 16 grs. of the former to 1 grain of the latter. The same elements form another compound, the persulphuret of hydrogen ; and in this the proportions are 32 of sulphur to 1 of hydrogen. Now  $32 = 16 + 16$ .

If, therefore, we know the weights of two bodies, B and C, which combine with a given weight of A, we also know the relative weights in which, or in multiples or submultiples of which, B and C will combine together.

Now oxygen is capable of uniting with all the other elements, (save perhaps with fluorine) ; and therefore if we ascertain by experiment the weights of the different elements which combine with a given weight of oxygen, the weights thus obtained will inform us, not only in what proportions (or their multiples) these elements combine with oxygen, but also in what proportions (or their multiples) they combine with each other, provided they are capable of doing so.

It is obviously of no importance what number we select to represent the standard weight of oxygen, to which the other elements are referred. On the Continent 100 is usually taken, and the combining numbers of the other elements are referred to oxygen as 100. In this country, for the sake of convenience in calculation, advantage has been taken of the fact that the combining weight or number of hydrogen is the smallest of all, and hydrogen has consequently been made the standard, with the number 1. Now as 1 of hydrogen is found to combine (in water) with 8 of oxygen, it is obvious that if hydrogen be represented by 1, oxygen will be represented by 8. Again, on the continental scale, oxygen being 100, hydrogen must be  $\frac{100}{8} = 12\cdot5$ , the proportion being preserved exactly the same. So that it is equally correct to say that water is composed of 100 grs. of oxygen, combined with 12·5 of hydrogen, and to say that water consists of 8 grs. of oxygen and 1 of hydrogen. In this work we shall use the hydrogen scale, but it is hardly necessary to point out that the numbers of the hydrogen scale, if multiplied by 12·5, are converted into those of the oxygen scale.

The numbers, then, attached to the names of the elements in the subjoined Table, are the results of experience, and merely represent the relative weights of the elements which (or multiples of them) combine with 8 of oxygen.

TABLE OF COMBINING PROPORTIONS, OR EQUIVALENTS.

| ELEMENTS.                       | Symbols. | Hydrogen.<br>= 1. | ELEMENTS.                    | Symbols. | Hydrogen.<br>= 1. |
|---------------------------------|----------|-------------------|------------------------------|----------|-------------------|
| Aluminium . . . . .             | Al       | 13·7              | Molybdenum . . . . .         | Mo       | 46                |
| Antimony (Stibium) . . . . .    | Sb       | 120·3             | Nickel . . . . .             | Ni       | 29·6              |
| Arsenic . . . . .               | As       | 75                | Niobium . . . . .            | Nb       |                   |
| Barium . . . . .                | Ba       | 68·5              | Nitrogen . . . . .           | N        | 14                |
| Bismuth . . . . .               | Bi       | 213               | Norium . . . . .             | No       |                   |
| Boron . . . . .                 | B        | 10·9              | Osmium . . . . .             | Os       | 99·6              |
| Bromine . . . . .               | Br       | 80                | Oxygen . . . . .             | O        | 8                 |
| Cadmium . . . . .               | Cd       | 56                | Palladium . . . . .          | Pd       | 53·3              |
| Calcium . . . . .               | Ca       | 20                | Pelopium . . . . .           | Pe       |                   |
| Carbon . . . . .                | C        | 6                 | Phosphorus . . . . .         | P        | 32                |
| Cerium . . . . .                | Ce       | 47                | Platinum . . . . .           | Pt       | 98·7              |
| Chlorine . . . . .              | Cl       | 35·5              | Potassium (Kalium) . . . . . | K        | 39·2              |
| Chromium . . . . .              | Cr       | 26·7              | Rhodium . . . . .            | R        | 52·2              |
| Cobalt . . . . .                | Co       | 29·5              | Ruthenium . . . . .          | Ru       | 52·2              |
| Columbium (Tantalum) . . . . .  | Ta       | 92                | Selenium . . . . .           | Se       | 39·5              |
| Copper (Cuprum) . . . . .       | Cu       | 31·7              | Silicon . . . . .            | Si       | 21·3              |
| Didymium . . . . .              | D        | 49·6              | Silver (Argentum) . . . . .  | Ag       | 108               |
| Erbium . . . . .                | E        | ?                 | Sodium (Natrium) . . . . .   | Na       | 23                |
| Fluorine . . . . .              | F        | 18·9              | Strontium . . . . .          | Sr       | 43·8              |
| Glucinum . . . . .              | G        | 26·5 ?            | Sulphur . . . . .            | S        | 16                |
| Gold (Aurum) . . . . .          | Au       | 197               | Tellurium . . . . .          | Te       | 64·2              |
| Hydrogen . . . . .              | H        | 1                 | Terbium . . . . .            | Tb       |                   |
| Iodine . . . . .                | I        | 127·1             | Thorium . . . . .            | Th       | 59·6              |
| Iridium . . . . .               | Ir       | 99                | Tin (Stannum) . . . . .      | Sn       | 59                |
| Iron (Ferrum) . . . . .         | Fe       | 28                | Titanium . . . . .           | Ti       | 25                |
| Lanthanum . . . . .             | La       | 47 ?              | Tungsten (Wolfram) . . . . . | W        | 95                |
| Lead (Plumbum) . . . . .        | Pb       | 103·7             | Uranium . . . . .            | U        | 217·2             |
| Lithium . . . . .               | Li       | 6·9               | Vanadium . . . . .           | V        | 68·6              |
| Magnesium . . . . .             | Mg       | 12·2              | Yttrium . . . . .            | Y        | 32·2              |
| Manganese . . . . .             | Mn       | 27·6              | Zinc . . . . .               | Zn       | 32·6              |
| Mercury (Hydrargyrum) . . . . . | Hg       | 200               | Zirconium . . . . .          | Zr       | 22·4              |

The number 39, attached to potassium,\* expresses the fact that 39 grains of potassium combine with 8 of oxygen, and 16 of sulphur : 8 and 16 being the numbers respectively attached to oxygen and sulphur.

These numbers further express the facts, that if we wish to convert 47 grains of oxide of potassium, composed of 39 of potassium and 8 of oxygen, into sulphuret of potassium, 16 grs. of sulphur will be required to displace the 8 of oxygen, and will give 55 grains of sulphuret.

We thus perceive that 16 grains of sulphur are the equivalent of 8 grains of oxygen. Hence the term "equivalent" is used as synonymous with combining proportion, and we shall in this work employ the term equivalent by preference.

When an element combines with oxygen in only one proportion, the equivalent of that element is the weight which combines with 8 (or on the other scale with 100) of oxygen.

\* Here the fractions, for convenience, are omitted.



Or we may calculate the equivalent from the compound, if there be one, of the element with chlorine.

Thus, in the oxide of potassium (potash), 39 grs. of potassium are combined with 8 of oxygen. If there were no other compound of potassium and oxygen, we should take 39 for the equivalent of potassium. But there is another compound of these elements, and in order to acquire certainty, we refer to the compound (there is but one) which potassium forms with chlorine. We find this to contain 39 grs. of potassium, and 35 of chlorine; and as 35 is the equivalent of chlorine, we conclude that 39 is the true equivalent of potassium.

Where an element combines with oxygen in several proportions, we are more uncertain. If the proportions of oxygen belong to the series of simple multiples, the equivalent is usually calculated from that compound which contains least oxygen, assuming that to contain an equivalent of oxygen.

Thus nitrogen forms 5 compounds with oxygen. In the first, 14 grs. of nitrogen are combined with 8 of oxygen; in the fifth, 14 grs. of nitrogen are united with 40 of oxygen. Taking the former, we conclude 14 to be the equivalent of nitrogen; but if we selected the other, then the equivalent of nitrogen would necessarily be five times smaller. On the ordinary view, we consider the fifth compound to consist of one equivalent of nitrogen = 14, and 5 equivalents of oxygen =  $8 + 5 = 40$ . But it will be seen that this is, to some extent, arbitrary; and that we might consider the fifth compound as formed of one equivalent of each, and the first as composed of one equivalent of oxygen, and 5 of nitrogen.

The usual system of equivalents, above explained, being consistent and uniform, as far as possible, is very convenient; but the student must remember, that while the combining proportions are fixed, it is, in any one compound, a matter of arbitrary choice, whether it be viewed as containing one or more equivalents of any element.

A very large proportion of elements, however, combine among each other according to laws so simple, that when we have assumed 8, for example, to represent one equivalent of oxygen, we need have no doubt as to the equivalents of the other elements.

In those compounds of one element with two or three proportions of another, where the quantities of the latter are not simple multiples, but belong to the series 3 : 5 : 7, much greater uncertainty prevails as to the equivalents. Thus, arsenic, antimony, and phosphorus, form compounds with oxygen, chlorine, and sulphur, belonging to this latter series; and

chemists are not fully agreed whether they ought to consider the quantity of arsenic, antimony, or phosphorus, which combines with 3 or 5 equivalents of oxygen, chlorine, and sulphur, as representing one equivalent, or two equivalents. The same doubt occurs in other cases: and we are guided, in such instances, chiefly by probabilities, and by the rule to avoid, as much as possible, fractions of equivalents. Thus, if we suppose the first oxide of arsenic to contain 1 equivalent of arsenic, and 1 of oxygen, the second must contain 1 equivalent of arsenic, and  $1\frac{2}{3}$  equivalents of oxygen. We, therefore, prefer to consider the first as formed of 1 eq. arsenic, and 3 eq. oxygen; and the second as formed of 1 eq. arsenic, and 5 eq. oxygen.

The equivalent of a compound body is the sum of the equivalents of its component parts. Thus, potash being composed of 1 eq. of potassium, 39, and 1 eq. of oxygen, 8, its equivalent is  $39 + 8 = 47$ . Sulphuric acid is composed of 1 eq. of sulphur, 16, and 3 eq. of oxygen, 24; and, consequently, its equivalent is  $40 = 16 + 24$ . As in the case of elementary bodies, the equivalents represent the combining proportions. Thus, the neutral sulphate of potash contains 47 grs. of potash, and 40 grs. of sulphuric acid. The law of multiples also applies to compound bodies; for there is another compound of sulphuric acid and potash, the bisulphate of potash, in which 47 grs. of potash are combined with 80 grs. of sulphuric acid, or 1 eq. of potash with 2 eq. of the acid.

The use of equivalents enables us to define more accurately some of the more important classes of compounds.

Oxygen acids are compounds of one or two equivalents of the metalloids, and of certain metals, with two or more equivalents of oxygen.

Oxygen bases are, without exception, compounds of metals with oxygen. In most cases, the base contains 1 eq. of the metal, and 1 eq. of oxygen; in a few bases there are two eq. of the metal, and 3 eq. of oxygen; and in one or two there are two eqs. of metal to 1 eq. of oxygen.

A neutral salt is a compound of 1 eq. of an oxygen acid, with 1 eq. of a base; or a compound of 1 eq. of a metal with 1 eq. of the radical of a hydrogen acid. Thus neutral sulphate of potash contains 1 eq. of sulphuric acid, and 1 eq. of potash; while common salt is composed of 1 eq. of sodium, and 1 eq. of chlorine.

A hydrogen acid is, in almost every case, composed of 1 eq. of hydrogen, and 1 eq. of a radical, simple or compound. Thus hydrochloric acid is composed of 1 eq. of hydrogen, and 1 eq. of

chlorine ; and hydrocyanic acid is formed of 1 eq. of hydrogen, and 1 eq. of the compound radical cyanogen.

The equivalent of an acid is that quantity which will form a neutral salt with one equivalent of a base ; and, in like manner, the equivalent of a base is that quantity which forms a neutral salt with one equivalent of an acid.

The equivalent of potash is 47. Now in order to form a neutral salt with 47 grs. of potash, 54 grs. of nitric acid must be added ; 54 is, therefore, the equivalent of nitric acid. Again, 40 is the equivalent of sulphuric acid ; and in order to form a neutral salt with 40 grs. of sulphuric acid, 31 grs. of soda are required. Hence, 31 is the equivalent of the base, soda or oxide of sodium. And in proof of this, we find that 31 of soda unite with 54 of nitric acid to form the nitrate of soda.

Since the equivalent of a compound body is the sum of the equivalents of its constituents, it follows, that if we know the equivalent of a compound and the relative proportions by weight of its component parts, we can calculate the *number* of equivalents of each element contained in the compound. For example, we find by analysis, that 100 grs. of hyposulphuric acid are composed of 44·59 grs. sulphur, and 55·41 grs. oxygen. We also find, by experiment, that the equivalent of hyposulphuric acid is 72. Now, in order to ascertain the number of equivalents of sulphur and oxygen contained in the acid, we first examine how much sulphur and oxygen are present in 72 grs. of the acid. It is clear, that if 100 grs. contain 44·59 of sulphur, 72 will contain 32 of sulphur ; and the remainder, 40, must be oxygen. But 32 is equal to 2 eq. of sulphur, the equivalent of sulphur being 16 ; and 40 is equal to 5 equivalents of oxygen, or 5 times 8. Hence the acid in question is composed of two eq. of sulphur, combined with 5 eq. of oxygen.

The rule for the above calculation is to ascertain the proportions of the elements in the equivalent number of the compound ; and as these proportions represent respectively the sums of the equivalents of the elements, to divide the numbers by the equivalents. In the above case, 32 (the proportion of sulphur in 72, the equivalent of the acid)  $\div 16 = 2$  eq. of sulphur ; and 40 (the proportion of oxygen in 72 of the acid)  $\div 8 = 5$  eq. of oxygen.

In cases where we have ascertained the proportions of the elements in a compound, but are ignorant of its equivalent or combining proportion, we cannot determine with certainty the absolute, but only the relative number of equivalents contained

in the compound. For example, it is shown by analysis, that 100 grs. of sugar of milk contain—

|          |           |        |
|----------|-----------|--------|
| Carbon   | . . . . . | 40.45  |
| Hydrogen | . . . . . | 6.61   |
| Oxygen   | . . . . . | 52.94  |
|          |           | <hr/>  |
|          |           | 100.00 |

But as sugar of milk enters into hardly any combinations, we cannot ascertain its combining proportion or equivalent, and thus it is of course impossible to tell how many equivalents of carbon, hydrogen, and oxygen, are contained in 1 eq. of sugar of milk. But we can ascertain the relative numbers of equivalents as follows :—Divide the weight of carbon in 100 parts of sugar of milk by the equivalent of carbon, which is 6 ;  $40.45 \div 6 = 6.74$ . Next, divide the weight of hydrogen in 100, which is 6.61, by the equivalent of hydrogen, which is 1 ;  $6.61 \div 1 = 6.61$ . Lastly, divide 52.94, the weight of oxygen in 100, by 8, the equivalent of oxygen,  $52.94 \div 8 = 6.61$ . Here, then, the relative numbers of equivalents of carbon, hydrogen, and oxygen, are represented by the numbers 6.74, 6.61, and 6.61 : or, making allowance for the unavoidable errors of manipulation, there is an equal number of equivalents of each. We cannot say whether sugar of milk contains 1, 2, 3, 4, 6, 12, or any other number of equivalents of each of its elements ; we only know that if 1 eq. of sugar of milk contains 12 eq. of carbon, it must likewise contain 12 of oxygen and 12 of hydrogen.

When a body, A, combines with B and C, and the number of equivalents of B and of C, which respectively unite with 1 or more equivalents of A is equal, the compounds A B and A C are said to correspond in constitution, or they are called corresponding compounds. Thus 1 eq. of potassium combines with 1 eq. of oxygen, and 1 eq. of potassium combines with 1 eq. of chlorine, and we say that chloride of potassium and protoxide of potassium (potash) are the corresponding chlorine and oxygen compounds of that metal.

When two compounds, A B and C D, respectively consist of an equal number of equivalents, they are said to be proportional compounds. Thus, oxide of potassium contains 1 eq. of oxygen and 1 eq. of potassium ; hydrochloric acid contains 1 eq. of hydrogen and 1 eq. of chlorine ; and we say that the composition of hydrochloric acid is proportional to that of oxide of potassium (potash).

When two proportional compounds mutually decompose each other, the resulting compounds are likewise proportional ; and we have a complete case of double decomposition. Thus 1 eq.

hydrochloric acid and 1 eq. oxide of potassium, act on each other, and give rise to water (1 eq. oxygen and 1 eq. hydrogen) and to chloride of potassium (1 eq. chlorine and 1 eq. potassium), which new compounds are obviously proportional. Any excess of either of the original compounds, beyond the 1 eq. required, remains undecomposed, and mixes with the new compounds.

When two bodies act on one another, which are not proportional, they may do so in the proportion of one equivalent of each, or in the proportion of 1 eq. of the one compound to 2 or more of the other.

In the former case there may be formed—

1. Two new compounds, not proportional to each other, but corresponding respectively to the two original compounds, or—

2. Two new proportional compounds, in which case one of the elements of one of the original compounds must be partially separated.

We may thus have

1.  $AB + CDD$  producing  $AC + BDD$

or,

2.  $AB + CDD$  producing  $AC + BD + D$

In the latter case there may be formed—

1. An equal number of new compounds, not proportional, but corresponding to the original compounds.

2. Two new compounds, proportional to each other, in which case an element has been partially separated.

3. Two new compounds, not proportional, and one of which does not even correspond to either of the original compounds. Here also an element has been partially separated.

We may thus have

1.  $A + 5B$  and  $5CD$  producing  $A + 5C$  and  $5BD$ .

2.  $A + 2B$  and  $2CD$  producing  $AC$ ,  $2BD$ , and  $C$ .

3.  $A + 5B$  and  $5CD$  producing  $A + 3C$ ,  $5BD$  and  $2C$ .

Numerous examples of these and of many similar modes of decomposition will occur in the course of this work. For the present, our space makes it necessary to confine ourselves to the general statements.

Under all circumstances, and in the most complicated chemical changes, the composition of the new products must admit, when expressed in equivalents, of a distinct relation being traced to the composition of the compounds from which these products have been derived. It is to the steady application of this principle to the investigation of the complicated decompositions

of organic compounds, that we must ascribe the amazingly rapid progress which has of late been made in organic chemistry.

It is obvious that where we are unable to trace the relation above-mentioned between the products and the substances which yield them, this must be looked upon as a proof that we do not yet fully understand the changes we are investigating; and that we are either mistaken in the composition which our analyses lead us to assign to one or more of the new compounds, or have overlooked some one or more of the products actually formed.

The laws of combination which have been briefly indicated in the foregoing pages, have been deduced from accurate observation, and are nothing more than an abridged expression of facts. They are consequently entirely independent of any theory or explanation of their causes which may be attempted. Neither is it necessary to attempt any such theory or explanation, since for all practical purposes, the facts alone are required.

But the human mind is never satisfied with observing and ascertaining facts, and deducing from them those general expressions which are called laws of nature. Man ever strives to account for, to explain, that which he has observed: and although his explanations never reach the essence of things, but only enable him to generalise to a greater extent, and to approach somewhat more nearly the Great First Cause of all, still it appears to be a law of his intellect, that he shall never cease from his attempts to explain, by reference to some simple principle, the complicated phenomena by which he is surrounded.

The facts of gravitation are well known, and entitle us to admit the law, that all material bodies have a tendency to move towards each other with a force which is proportional to their masses, and which varies inversely as the squares of their distances. To account for this, we are in the habit of assuming the existence of a certain force which we call the attraction of gravitation. But we know nothing of the nature of this force and, assuming its existence, it is only known to us by its effects. Nor does the assumption enable us to understand *how in what way*, it acts in attracting masses of matter towards each other.

But if we assume the existence of such a force, acting according to the above law, then we can deduce, as necessary inferences from these data, all the phenomena which have been observed, and many which have not been observed, but which we are thus enabled to anticipate. There is, therefore, an obvious advantage in assuming the existence of this supposed

cause, as we are thus enabled to remember and to classify the phenomena much better than in the form of a dry catalogue of facts, not attached to any common idea.

If, in like manner, we seek for some hypothesis, which shall account for the facts of combination in definite and multiple proportions, the first obvious conclusion is, that the cause of these phenomena must be intimately connected with the mechanical constitution of matter. But since our senses are not capable of directly taking cognisance of the ultimate physical constitution of matter, and since the ultimate causes of natural phenomena are also beyond the reach of our senses, we must have recourse to induction from facts, or to some hypothesis regarding the constitution of matter, which may serve to explain the phenomena.

Different opinions have been held as to the constitution of matter; but two in particular have prevailed. According to one, matter is susceptible of being divided *ad infinitum*: according to the other, matter is formed of particles, which are indeed very minute, far too minute to be cognisable by our senses; but which still possess a definite size, and cannot be divided. They are hence called *atoms*.

Now it is very remarkable, that if we assume the latter view, or that which is called the atomic constitution of matter, to be correct, and if we further assume that the individual atoms of different elements possess different weights, but always the same weight in the same element, we can, from these data, deduce all the facts of combination in definite and multiple proportions. This is the theory proposed by Dalton—The Atomic Theory.

No other hypothesis hitherto proposed is capable of explaining the phenomena; and therefore in the present state of our knowledge, and until a better explanation shall be given, we may admit the atomic theory. It is to be observed, however, that we have no positive proof of its truth, nor are we likely to obtain such proof. On the other hand, the discovery of any fact inconsistent with the atomic theory would compel us to reject it, even if we had no other theory to supply its place. But whether the atomic theory be admitted or not, the facts of combination in definite and multiple proportions remain unaffected.

#### ATOMIC THEORY.

According to the atomic hypothesis, therefore, matter is composed of certain minute, indivisible particles, or atoms; and consequently cannot be divided infinitely. We may divide

a mass of matter to a very great extent, far beyond the point at which our senses cease to be able to follow ; but still there is a limit to divisibility, and we should reach that limit if we succeeded in dividing so far that the resulting particles were the individual atoms.

Here it may be observed, that the partisans of the opinion according to which matter is infinitely divisible argue thus : There is no conceivable particle of matter so small that we cannot conceive it to be divided into two halves, and so on *ad infinitum* : therefore there is no limit to the divisibility of matter.

Now, while we admit that there is no limit to *our conception* of the divisibility of matter, this does not prove that there may not be a limit, in point of fact, to its actual divisibility. For, let us consider a moment what division really is ; and we shall find that it can only be defined as the separation of one portion of matter from others. Now as matter, in its usual forms, undoubtedly consists of particles held together, more or less firmly, by cohesion, it is plain that we can easily, by overcoming cohesion, separate those particles from each other ; and this is ordinary division.

But, on the atomic hypothesis, each of these visible ordinary particles is, like the original mass, formed of still smaller particles cohering together, but, in neither case, in absolute contact. Indeed the phenomena of expansion by heat, and contraction by cold, demonstrate that the particles of matter are not in absolute contact ; in other words, an ordinary mass of matter may be defined as *a portion of space not entirely filled with matter*.

Let us now define an atom as *a minute portion of space entirely filled by matter*, and we see at once that such a mass cannot possibly admit of division. It is strictly a unit, and as division implies separation of one unit from another, it is here evidently impossible. It is not meant that we can prove this to be the nature of atoms, for we cannot even prove their existence : but the object of the above illustration is to show that we can *conceive* the existence of an indivisible particle, and therefore that the argument above described in favour of the infinite divisibility of matter is not necessarily conclusive.

Such a particle or atom as has now been defined, or, in other words, a single portion of matter entirely filling the space bounded by its circumference, cannot be cut in two, like a mass of matter, for there is no interstice into which, as in ordinary matter, the edge of a cutting instrument can penetrate ; and it cannot, being a unit, be separated from itself.



It cannot be crushed to powder, for the particles of a powder existed previously as distinct particles, in the solid mass of matter, and were only separated by the force employed. It cannot be drawn out like metal into wire, or beaten out into thin leaves : for both drawing out and beating out are merely new *arrangements* of a plurality of particles, and we have here only a unit.

Moreover, such a particle or atom would, in all probability, be spherical, since no reason can be assigned why one dimension should exceed another. It would no doubt be opaque ; for transparency is the result of the passage of light through the vacant spaces between the particles of matter : and colourless, because colour depends on the action of the particles of matter on light ; and it would be perfectly hard.

In short, it is evident that we can imagine indivisible atoms to exist ; and that the physical properties of matter are not in any degree inconsistent with the idea that it is made up of such atoms.

Before proceeding it is proper to repeat that we have no certainty that matter is composed of particles or atoms, and that, in fact, we know nothing with certainty as to the intimate nature, or essence of matter. It must never be forgotten, that all that we know about matter is its properties ; that is, we observe certain properties, such as form, size, weight, colour, hardness, transparency, and the like, and further we see that one kind of matter acts on another, combining with it, or dissolving it, or corroding it, or changing it in a variety of ways. But we are utterly unable to say *what it is* that possesses these properties, or in other words *to what* these properties are attached or belong. The atomic hypothesis assumes or supposes that they belong to certain minute particles or atoms, the most universal properties, such as impenetrability and weight, belonging to the individual atoms, and the secondary properties, such as colour, taste, hardness, elasticity, &c., depending on the mode of grouping or arrangement of the atoms. And this is possible, although it has never been, and most probably never will be, demonstrated. But it is also possible, and many philosophers incline to this opinion, that there are no such atoms considered apart from their properties, which properties are all that we really know. It may be that what have been called atoms are mere points in space, which are the centres of various forces of attraction and repulsion. For all the properties of matter, without exception, may be reduced to attractions and repulsions. Weight is an attraction ; so is chemical affinity ; heat appears to be a repulsion ; and so of all the others. Now

if we imagine certain forces of attraction and repulsion, acting from a centre, and nothing more than these forces, we have all the known conditions of an atom, that is, of matter. We are apt to fancy that there must be a something distinct from the properties of matter, a substratum to which they are attached, and we cannot at first readily abstract, and regard the known forces alone as constituting what we really know. We imagine that that which has weight must have a something, a substance, distinct from weight; but of this we know absolutely nothing: and the forces above alluded to, if grouped round centres, would produce exactly the same results as we actually observe without any such substratum as is supposed. When we perceive the weight of a mass, or the resistance it opposes to external force, we naturally attribute these properties to a being which we call matter; but, in reality, weight is only an attraction, and resistance only a repulsion. But while so little is really known of the nature of matter, it is obvious that on the atomic hypothesis we can readily understand and classify the facts we observe; it is equally certain that the centres of force, on the other hypothesis, exactly correspond in these results, to the atoms of the former one, and, if once admitted, would serve equally well for the purposes of explanation. But to proceed.

The atomic hypothesis goes on to assume that the atoms of the different elements possess different weights, but that those of the same element possess invariably the same weight.

The third assumption is, that when one element unites with another, the atoms of the two respectively combine. Thus, an atom of A combines with an atom of B, to form an atom of the compound AB. Or, two atoms of A unite with three atoms of B, to form an atom of the compound AABBB.

A distinction must here be made between simple or elementary atoms and compound atoms. It is obvious that an atom of AB, if it contain an atom of A and an atom of B, may be decomposed, and A separated from B. AB is, therefore, not an atom in the fullest sense of the word. But A cannot be separated from B by mechanical means, or otherwise than by chemical agency; so that, in a mechanical sense, AB is an atom, although a compound one. A mass of the compound AB is made up of mechanically indivisible, but chemically divisible, particles of AB, each of which, although it may be called an atom, contains an atom of each of the elements.

The *absolute* weight of the atoms of the different elements is altogether unknown. If, indeed, we had any means of ascertaining the number of atoms in a given weight of any

element, in one grain for example, we should know the actual weight of each atom ; but this is for the present beyond our power.

But we know the relative weights of two elements which combine to form a given compound ; and, therefore, if we assume that the compound contains one atom of each element, we know at once the *relative* weights of the atoms of those elements. Thus, 8 grs. of oxygen unite with 1 gr. of hydrogen to form 9 grains of water ; and we assume that the water contains 1 atom of each element or an equal number of atoms of each. In that case it is clear that the relative weights of the single atoms must be the same as those of what are assumed to be equal numbers of each ; and, consequently, 1 atom of oxygen will be eight times heavier than 1 atom of hydrogen. If the 8 grs. of oxygen contain 8,000,000 of atoms, then one atom of oxygen would weigh  $\frac{8}{10000000}$  of a grain, and one atom of hydrogen  $\frac{1}{10000000}$  of a grain. But although we shall most probably never know the actual number in a given weight, or the absolute weight of the atoms, we are not the less sure that, if matter be composed of atoms differing in weight for each element, and if water be formed by the union of an equal number of atoms of oxygen and hydrogen, then 1 atom of oxygen must be 8 times heavier than 1 atom of hydrogen.

These numbers, then, express merely the relative weights of these atoms : on the above assumptions, 8 represents the weight of an atom of oxygen, if an atom of hydrogen be supposed to weigh 1 : and 12·5 will represent the weight of an atom of hydrogen, if an atom of oxygen be supposed to weigh 100. It is evident that any other numbers might be used, provided the ratio, in this case that of 8 to 1, were kept up.

It is now easy to see, that the atomic hypothesis, if assumed, at once explains all the facts of combination in definite and multiple proportions. As has already been remarked, no other hypothesis yet proposed is capable of doing this ; and, therefore, while we must not lose sight of the fact that the atomic hypothesis has not been, and indeed probably never will be, demonstrated to be true, we are justified in adopting it, until it shall be proved to be false, or until a better one shall be proposed in its stead.

It will be observed that the weights of the atoms, or atomic weights, as they are termed, coincide with the equivalent numbers previously given. When, therefore, the term atomic weight is used, it is not as implying the established truth of the atomic theory, but only as a convenient synonym for the term equivalent, or for that of combining proportion. Whichever

name we use, it must never be forgot that the facts remain unchanged, and are independent of all hypothesis. 9 grains of water invariably contain 8 of oxygen and 1 of hydrogen, whether we speak of the combining proportions, the equivalents, or the atomic weights of oxygen and hydrogen being represented by the numbers 8 and 1. The two former expressions have the advantage of simply expressing the fact without any allusion to hypothesis, and are, therefore, strictly speaking, preferable ; but the latter is much used, and may safely be employed when properly defined.

In this country, the terms equivalent and atom have been from the beginning held to be entirely synonymous. On the continent, this has not been the case ; for the equivalent of many elements, such as hydrogen, chlorine, &c., has been there assumed to contain 2 atoms ; and hence the atomic weight of hydrogen, for example, has been on the continent one half of that adopted here.

This is a matter which is, to a great extent, arbitrary, and only affects the mode of viewing and representing the composition of certain compounds. Thus continental chemists, admitting as we do that 9 grains of water contain 8 of oxygen and 1 of hydrogen, consider water to be composed of 1 atom of oxygen and 2 atoms ( $=$  1 equivalent) of hydrogen ; they, consequently, give to hydrogen the atomic weight of 0.5, that of oxygen being 8 ; or 6.25, that of oxygen being 100.

It is not easy to decide whether water be composed of 1 *atom* of each element, or of 1 *atom* of oxygen to 2 *atoms* of hydrogen. But as both parties agree that water contains 1 *equivalent* of each element, it is obvious that the system adopted in Britain by which equivalent is made entirely synonymous with atom, has the very great advantage of superior simplicity : and that system will, therefore, be followed in this work. Within the last few years, several of the most distinguished chemists on the continent have adopted the British system in this respect, and there is little doubt that it will, ere long, become universally prevalent.

The table of equivalents, formerly given, is therefore, at the same time, a table of atomic weights. It is now time to give rules for the use of that table, and particularly for the use of the abbreviations or symbols there attached to the elements, in the construction of formulæ.

## CHEMICAL SYMBOLS AND FORMULÆ.

These have nothing in common with algebraical symbols and formulæ. They are mere abbreviations, and are intended to express only the arithmetical operations of addition and subtraction. Various systems have been given to the world : but that which has finally obtained the most extensive currency among the chemists of the day, is one proposed by Liebig and Poggendorff, which we now proceed to explain.

The symbol of an element, standing alone, signifies 1 atom, or equivalent, of the element. Thus O stands for 1 atom of oxygen, H for 1 atom of hydrogen, and Fe for one atom of iron (ferrum).

A symbol, with a small figure below and to the right, signifies as many atoms of the element as the figure expresses. Thus  $O_2$  means 2 atoms of oxygen,  $S_5$ , 5 atoms of sulphur. Some writers place the small figure above instead of below, as  $O^5, S^2$  : But we prefer the former plan, as not recalling the symbols of the powers in algebra.

Two symbols joined by the sign +, or simply placed together, signify a compound of 1 atom of each element. Thus  $H + O$ , or simply  $HO$ , means water, a compound of 1 atom of hydrogen, and 1 atom of oxygen.

If a figure be attached, as above, to either or both symbols, it multiplies that symbol only to which it is attached. Thus  $MnO_2$  is the symbol for peroxide of manganese, a compound of 1 eq. of manganese and 2 eq. of oxygen.  $CuO$  is the symbol of suboxide of copper, composed of 2 eq. of copper and 1 eq. of oxygen.  $Fe_2O_3$  is the symbol of sesquioxide of iron, which contains 2 eq. of iron and 3 eq. of oxygen.

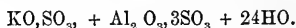
When a compound, formed of two or more compounds, is to be expressed, the compounds which combine are joined, either by a + sign or by a comma. Thus  $HO + SO_3$ , or  $HO, SO_3$ , both signify hydrated sulphuric acid, a compound of 1 eq. of water and 1 eq. of dry sulphuric acid.

A large figure, printed on the same level as the symbol, and to the left of it, multiplies every symbol, as far as the next comma, or the next + sign ; or it multiplies all within brackets if placed before them. Thus  $2HO$  means 2 atoms of water,  $2SO_3, KO, HO$  represents bisulphate of potash, a compound of 2 eq. of sulphuric acid, 1 eq. of potash, and 1 eq. of water. It might also be written  $2SO_3 + KO + HO$ . But the following,  $2(SO_3, KO, HO)$  would signify 2 eq. of a compound which was formed of 1 eq. of sulphuric acid, 1 eq. of potash, and 1 eq. of water.

When a compound contains 3 or more elements, the symbols are written simply one after the other, with the necessary figures. Thus, sugar is represented by  $C_{12}H_{10}O_{10}$ : that is 12 eq. of carbon, 10 eq. of hydrogen, and 10 eq. of oxygen. Alcohol is  $C_4H_6O_2$ .

If we wish to show that any compound of three or more elements really contains two compounds, it is expressed in the following manner: alcohol,  $C_4H_6O_2$ , when viewed as a compound of ether and water becomes  $C_4H_5O + HO$ . Benzoic ether,  $C_{18}H_{10}O_4$ , becomes  $C_{14}H_5O_3$  (benzoic acid) +  $C_4H_5O$  (ether).

In this way we find it quite easy to express in symbols the composition of the most complicated substances. For example, crystallised alum is composed of 1 eq. of neutral sulphate of potash, 1 eq. of tersulphate of alumina, and 24 eq. of water of crystallisation. This is expressed in symbols, as follows:



And this abbreviated expression contains, in a line, in addition to the general information concerning alum printed above, more information as to details than could be given in a page of print. It informs us, for example, that alum contains 4 eq. of sulphuric acid, of which 1 is combined with 1 eq. of potash, and 3 with 1 eq. of alumina: that alumina is a sesquioxide of aluminium: that 1 eq. of alum contains 1 eq. of potassium, 2 eq. of aluminium, 4 eq. of sulphur, 24 eq. of hydrogen, and 40 eq. of oxygen, &c. &c. &c.

There are, besides the direct information thus conveyed by symbols, two most important uses to which they are applied.

The first is, to render easily intelligible the view taken by a writer of any chemical change, however complicated. This is done by means of a formula or equation: in which all that is essential is, that the sum of the various symbols should be the same on both sides. Thus to take an example previously described in words (at p. 21,) the action of oxide of potassium on hydrochloric acid. This is expressed in a formula as follows:

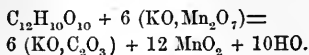


Here the symbols on the left are those of the bodies which act on each other, oxide of potassium and hydrochloric acid: while those on the right are the symbols of the new compounds produced, water and chloride of potassium.

Or, to take a more complicated case.

Sugar,  $C_{12}H_{10}O_{10}$ , when acted on by 6 eq. of hypermanganate of potash,  $KO, Mn_2O_7$ , gives rise to 6 eq. of oxalate of

potash,  $\text{KO}, \text{C}_2\text{O}_3$ , 12 eq. of peroxide of manganese,  $\text{MnO}_2$ , and 10 eq. of water,  $\text{HO}$ . All this is briefly and clearly expressed by the equation,



The second very important use to which these equations are applied is that of calculating the quantities of the different substances which must be employed, in order to operate as economically as possible, and likewise the weight of the products which ought to be obtained. Thus, in the last example, we wish to know what proportions of sugar and hypermanganate of potash ought to be used, that nothing of either should be wasted : and also how much oxalate of potash, peroxide of manganese and water will be obtained. By means of the above equation, and the table of atomic weights, we can easily make all these calculations. Since the equivalent or atomic weight of a compound is the sum of those of its elements, it is obvious that the equivalent of sugar is equal to the sum of 12 eq. of carbon + 10 eq. of hydrogen + 10 eq. of oxygen. Now by the table, the equivalent of carbon is 6, that of hydrogen 1, that of oxygen 8. Hence the equivalent of sugar =  $6 \times 12 + 1 \times 10 + 8 \times 10 = 72 + 10 + 80 = 162$ . In like manner the equivalent of hypermanganate of potash is found to be, in round numbers, 160. For every 162 parts, therefore, of sugar, we must employ 6 times  $160 = 960$  parts of hypermanganate of potash. The whole materials employed amount to 1122.

On the other hand, we obtain of oxalate of potash, the equivalent of which is (in round numbers) 84, 6 equivalents = 504 ; of peroxide of manganese, the equivalent of which is 44, 12 equivalents = 528 ; and of water, the equivalent of which is 9, 10 equivalents = 90 ; the whole products amounting, as before, to 1122.

It is hardly possible to exaggerate the value of so easy a method of representing chemical changes, and of making all the necessary calculations connected with them. Every chemist, and every student of chemistry, ought to be quite familiar with the use of chemical formulæ ; and, indeed, without this knowledge it is almost impossible to read chemical writings. The use of formulæ enables the writer so easily to put before his readers, in a very small space, any conceivable view of the phenomena, such as might require pages to explain in words, that they are now universally employed.

Even in the commonest use of symbols and atomic weights, that, namely, of expressing the composition of any compound,

the advantage derived from their employment is immense. Thus, previous to the invention of tables of atomic weights, chemists could only express the composition of a compound by giving the proportions of the elements contained in 100 parts. For example, water, the protoxide of hydrogen, was found to consist of Hydrogen, 11.11; and Oxygen, 88.88, in 100 parts; while the deutoxide of hydrogen was found to consist of Hydrogen, 5.89; and Oxygen, 94.11, in 100 parts. It is very difficult for the memory to retain these numbers with accuracy, even in the case of a few such compounds; how much more so, then, must it be to remember the composition of the numerous bodies with which the chemist is constantly occupied?

If, however, we have recourse to symbols, we have only to express the composition of water by  $\text{HO}$ , and that of the deutoxide of hydrogen by  $\text{HO}_2$ ; and referring to the table of atomic weights, we find that the former contains 1 part, by weight, of hydrogen to 8 of oxygen, and the latter, 1 of hydrogen to 16 of oxygen. Even if we could not retain these latter numbers, we should thus still derive great benefit from the use of symbols; but the fact is, that we soon learn the atomic weights of the more important elements, and are not compelled to have recourse to the table for them.

But this is not all; for in the numbers, as given in 100 parts, we can trace no relation; and, consequently, if we commit them to memory, must do so as bare numbers. In the symbols, on the contrary, we see at a glance that the same quantity of hydrogen which, in water, is combined with a given weight of oxygen, is combined with double that weight in the deutoxide of hydrogen; and we are thus supplied, not only with a fact, in itself of the highest value, but also with a link by which the composition of two substances is associated in the memory, and is therefore retained with facility.

Before quitting this part of the subject, it is well to point out two results which follow from the atomic theory.

The first is, that since, by definition, an atom is that which cannot be divided, there cannot be formed a compound of  $\frac{1}{2}$  an atom, or equivalent, of one element, and  $\frac{1}{2}$  an atom (or any fractional number of atoms, as  $1\frac{1}{2}$ ,  $2\frac{1}{2}$ , &c.) of another element. Should such proportions appear to exist, they must be so expressed as to get rid of fractions, otherwise they imply a contradiction in terms. Thus, for example, iron combines with oxygen in two proportions. In the first compound, or protoxide of iron, 28 parts (1 eq.) of iron are combined with 8 parts, or 1 eq., of oxygen. We, therefore, assume this compound to contain 1 atom of each element, and express it in



symbols by  $\text{FeO}$ . In the other oxide, or peroxide of iron, 28 parts, or 1 eq., of iron are found to be combined with 12 parts of oxygen. Now, 8 being 1 eq. of oxygen, 12 must be  $1\frac{1}{2}$  eq. But as it would be absurd to call this oxide a compound of 1 atom of iron and  $1\frac{1}{2}$  atom of oxygen, we get rid of the fraction by doubling both numbers and we represent the peroxide of iron by  $\text{Fe}_2\text{O}_3$ . Here the proportion is still that of 1 to  $1\frac{1}{2}$ , but the absurdity of dividing an atom is avoided. It is obvious that the atomic weight of the compound is double what it would be if we had retained the fraction : for  $\text{Fe}_2 = 56$ , and  $\text{O}_3 = 24$  : and  $56 : 24 :: 28 : 12$ . As the proportion is still that of 1 to  $1\frac{1}{2}$  atom, although there are, in reality, 2 to 3, this compound is frequently called sesquioxide of iron, from *sesqui*, a prefix signifying one and a half. The prefix *sesqui* is used in many similar cases, precisely in the same way.

Of course, where analysis indicates the proportion of 1 atom of A to  $2\frac{1}{2}$  or  $3\frac{1}{2}$  of B, we, in like manner, to avoid fractions, express these proportions by 2 to 5, or by 2 to 7. The symbol for hyposulphuric acid is  $\text{S}_2\text{O}_5$ ; that of hypermanganic acid is  $\text{Mn}_2\text{O}_7$ .

The second result or corollary from the atomic theory, is, that when two compounds having a common element unite together, the amount of the common element in the equivalent of the one is, to its amount in the equivalent of the other, in a ratio which may be expressed by whole numbers. Thus, potash is composed of potassium and oxygen, sulphuric acid of sulphur and oxygen. Here oxygen is the common element. Now, in an equivalent of potash,  $\text{KO}$ , there is one atom of oxygen = 8. In an equivalent of sulphuric acid,  $\text{SO}_3$ , there are 3 atoms of oxygen = 24 : and it is obvious that the oxygen in the latter is to that in the former as 3 : 1. This relation is at once seen in the formula of the compound, sulphate of potash, which is  $\text{KO}, \text{SO}_3$ ; and it prevails necessarily in all neutral compounds of sulphuric acid with bases which have an analogous constitution. In nitrate of potash,  $\text{KO}, \text{NO}_5$ , the ratio is different, being as 5 : 1. When an acid, such as sulphuric acid, forms a neutral salt with a base of a constitution different from that of potash, as for example, with sesquioxide of iron, the relation of 3 to 1 is still kept up; for the neutral sulphate of sesquioxide of iron is  $\text{Fe}_2\text{O}_3, 3\text{SO}_3$ . In a compound not neutral, such as  $\text{Fe}_2\text{O}_3, \text{SO}_3$ , which represents the basic sulphate of sesquioxide of iron, the relation is different, being that of 3 : 3 or 1 : 1; but still it is capable of being expressed in whole numbers.

## COMBINATION BY VOLUMES.

It has been already stated that the gaseous form is caused by the predominance of the repulsion due to heat over the force of cohesion. In each substance, the change from the liquid form, in which these opposing forces are exactly balanced, to the form of gas, takes place at a temperature which is always the same for the same substance, as long as the pressure remains unchanged, but differs in different bodies. Now as this temperature, called the boiling point, is nothing else than the point at which the repulsion due to heat at last overcomes cohesion, and separates the particles to a much greater distance than before, giving rise to the property of elasticity, it is plain that at this point there must be a definite relation between the *volume* of the body converted into gas, and its weight, a relation which is more easily traced in the gaseous than in the liquid or solid form; because there is but one mode of gaseous existence, while solids, and even liquids may assume a variety of forms, depending not only on cohesion, but also on the tendency to crystallise, and other analogous forces, which interfere and complicate the results. For example, if we compare the volumes of two solid bodies, we shall find that equivalent weights may occupy widely different volumes, if it should happen that the one is crystallised and the other in the shape of an amorphous, irregular, and porous mass. But when two gases are compared at the same temperature, as the distance between the particles of both is the same, we find the very simplest relation between their volumes and their weights.

Thus, we find that when two gaseous bodies combine together, it is always in such proportions, by volume, that 1 volume of the one gas combines with one or two or more volumes of the other; and if the resulting compound be gaseous, its volume bears some simple ratio to those of its elements. Thus, 1 vol. of hydrogen combines with 1 vol. of chlorine, to produce 2 vols. of hydrochloric acid; and 2 vols. of hydrogen combine with 1 vol. of oxygen to form 2 vols. of the vapour or gas of water. It is evident, that where two gases combine in several proportions, the law of multiple proportions must prevail in regard to the volumes as well as in regard to the weights. For example, in the five compounds of nitrogen and oxygen formerly mentioned, 2 vols. of nitrogen are combined with 1, 2, 3, 4, and 5 vols. of oxygen.

The volume of the compound is in all cases either equal to the sum of the volumes of its component gases, or less than that sum; in the latter case condensation has taken place. It follows

that 1 vol. of a compound gas contains either 1 vol. of each of its constituents, or a multiple or a submultiple of a volume of one or both. It is easy to see that there must be a relation between the volume and the weight of gaseous elements, since the law of definite proportions can be traced in both. Since water, for example, is composed of 8 parts *by weight* of oxygen to 1 of hydrogen, and of 2 parts *by volume* of hydrogen to 1 of oxygen, it must be possible to construct a table of combining volumes, as well as a table of atomic weights; and in fact this may be done in regard to all those elements which may be made to assume the form of gas, and even in regard to some which cannot be obtained in that form, but which combine with gaseous elements to form gaseous compounds.

If the weight of a given volume of oxygen be called 1.000, it will be found that an equal volume of hydrogen will weigh sixteen times less, or 0.0625; and these numbers will represent the relative specific gravities of these gases. But we already know that in water 1 vol. of oxygen is combined with 2 vols. of hydrogen: or, taking the specific gravities, 1.000 oxygen with  $2 \times 0.0625 = 0.125$  of hydrogen. Now these latter numbers are precisely the atomic weights or equivalents of oxygen and hydrogen, oxygen being made the standard, and = 1.000. Again, 1 vol. of hydrogen combines with 1 vol. of chlorine to form hydrochloric acid. Now, if 1 vol. of hydrogen as above, be represented as weighing 0.0625, 1 vol. of chlorine will be found to weigh 2.25; and these numbers are to each other precisely in the ratio of the equivalents of the two gases, which, on the oxygen scale, are 12.5 and 450, or on the hydrogen scale, 1 and 36.

It was for a long time supposed, especially among continental chemists, that equal volumes of the simple gases contained equal numbers of atoms. Were this the case, the specific gravities of the gases compared to oxygen as a standard, would of necessity coincide with the atomic weights as compared with the same standard; and would at all events, whatever standard might be employed, bear the same ratio to each other. Specific gravity in the gaseous form and atomic weight would then be synonymous.

Experiment, however, has demonstrated that this is not the case; but that, while an equivalent of one element is represented by one volume of its gas, two volumes are required to make an equivalent in some cases; and one-half volume, one-third volume, or even less, in others. In the following table will be found the specific gravities or the weights of equal volumes of such elements as admit of their specific gravities being either directly taken or calculated. In the first column

are given the usual specific gravities compared to atmospheric air, as the standard : in the second the specific gravities compared to hydrogen as the standard, in order to show the relation to the atomic weights :—

| Gas or Vapour.        | Specific Gravities. |               | Chemical Equivalents. |            |
|-----------------------|---------------------|---------------|-----------------------|------------|
|                       | Air = 1.            | Hydrogen = 1. | By Vol.               | By Weight. |
| Hydrogen . . . . .    | 0·0690              | 1·00          | 100                   | 1·00       |
| Nitrogen . . . . .    | 0·9727              | 14·00         | 100                   | 14·00      |
| Carbon (hypothetical) | 0·4213              | 6·00          | 100                   | 6·00       |
| Chlorine . . . . .    | 2·4700              | 35·50         | 100                   | 35·50      |
| Iodine . . . . .      | 8·7011              | 127·10        | 100                   | 127·10     |
| Bromine . . . . .     | 5·3930              | 80·00         | 100                   | 80·00      |
| Mercury . . . . .     | 6·9690              | 101·00        | 200                   | 202·00     |
| Oxygen . . . . .      | 1·1057              | 16·00         | 50                    | 8·00       |
| Phosphorus . . . . .  | 4·3273              | 64·00         | 25                    | 16·00      |
| Arsenic . . . . .     | 10·3620             | 150·00        | 25                    | 37·50      |
| Sulphur . . . . .     | 6·6480              | 96·00         | 16·66                 | 16·00      |

It will be observed that the numbers in the second column are not the same in all cases as the equivalent numbers of the elements ; but many of them are so, and in these cases a volume represents an equivalent. The other numbers are multiples by a whole number of the equivalent, oxygen being represented, for example, by  $16 = 2 \times 8$ , and sulphur by  $96 = 6 \times 16$ . This shows that if an equivalent of hydrogen, chlorine, be represented by 1 vol., an equivalent of oxygen is represented by  $\frac{1}{2}$  vol., and an equivalent of sulphur by  $\frac{1}{6}$  vol.

The knowledge of the proportions by volume according to which bodies combine, and of the specific gravity of gaseous bodies, enables us to answer a great many questions, and decide a great many doubtful points in Chemistry. Thus—

1. If we know the specific gravity of two simple gases and the proportions by volume in which they combine, we can calculate the composition, by weight, of the compound. Thus, 2 vols. of hydrogen combine with 1 vol. of oxygen to form water. Now, the Sp. G. of hydrogen (Air=1·000), is 0·0694, and that of oxygen is 1·1111, nearly. Therefore water is composed, by weight, of  $0·0694 \times 2 = 0·1388$  of hydrogen, and 1·1111 of oxygen.

2. If we know the volumes of the elements of a compound, and their specific gravities, and the volume of the compound, we can calculate the Sp. G. of the compound. To take the same example, 2 vols. of hydrogen, Sp. G. = 0·0694, and 1 vol. of oxygen, Sp. G. = 1·1111, combine to form 2 vols. of vapour

of water. Now the vapour of water must weigh as much as the oxygen and hydrogen taken together, that is,  $0.0694 \times 2 + 1.1111 = 1.2499$ . But as this represents the weight of 2 vols. of vapour of water, the weight of 1 vol. of vapour of water (or the specific gravity) must be  $1.2499 \div 2 = 0.6249$ .

3. If we know the volume and the Sp. G. of one of the two elements of a binary compound, and the Sp. G. of the compound itself, we can calculate the composition, by weight, of the compound. Thus, 1 vol. of carbonic acid gas contains 1 vol. of oxygen; the Sp. G. of carbonic acid gas is 1.5239, and that of oxygen as before is 1.1111. Subtracting the latter number from the former, we have 0.4128, which must represent the weight of carbon united with 1.1111 of oxygen; and this is the composition, by weight, of carbonic acid gas.

4. If we know the specific gravity of a compound and its composition by weight, we can calculate the composition by volume. Example—by experiment the Sp. G. of the vapour of aldehyde (the weight of 1 vol.) was found to be 1.532; and the analysis of the compound showed that its composition by weight was carbon 55.024, hydrogen 8.983, and oxygen 35.993, in 100 parts. Now, in order to ascertain the composition by volume, let us calculate the proportions of carbon, hydrogen, and oxygen in 1.532.

|                      |                  |               |         |
|----------------------|------------------|---------------|---------|
| If 100 parts contain | 55.024 carbon,   | 1.532 contain | 0.84279 |
| „                    | „ 8.983 hydrogen | „             | 0.13760 |
| „                    | „ 35.993 oxygen  | „             | 0.55130 |

Now, the specific gravity or weight of 1 vol. of carbon is hypothetical or calculated: it is assumed to be 0.42139 (see table): 1 vol. of hydrogen weighs 0.0694, and 1 vol. of oxygen weighs 1.1111. It is easy to see, therefore, that 1 vol. of the vapour of aldehyde contains:—

|                           |           |         |
|---------------------------|-----------|---------|
| 2 vols. vapour of carbon  | . . . . . | 0.84279 |
| 2 vols. hydrogen          | . . . . . | 0.13880 |
| $\frac{1}{2}$ vol. oxygen | . . . . . | 0.55550 |

It is obvious, therefore, that the knowledge of the volumes in which gaseous bodies combine, and of their specific gravities, is of great value to the chemist: but we must not forget that we have no evidence that equal volumes of different elements contain an equal number of atoms; or, in other words, that the term volume may be substituted for atom or equivalent, as was at one time supposed. On the contrary, all the recent researches on this point go to prove that, in the case of many elements, a volume corresponds to two or more equivalents.

There is reason to believe that the want of correspondence

between the combining volumes of bodies in the gaseous state, and their combining weights, just alluded to, may depend on the circumstance that many, possibly all elements, are capable of existing in more than one state, or, as it is called, more than one allotropic form. We shall see that sulphur, phosphorus, carbon, silicon, and various metals, occur in forms which could hardly be supposed to belong to the same element; and it is quite conceivable, that this peculiarity may not be confined to the solid state, but that the same element may occur in two or more different gaseous forms, having, of course, different specific gravities. By the researches of Berzelius it appears that when sulphur and phosphorus combine, which they do in many proportions, the peculiar properties of these compounds seem to be connected with the different allotropic conditions of these two elements. Again, there are not only three solid forms of sulphur, but apparently also three liquid forms, in all probability corresponding to the solid ones. Is it not therefore probable, that the ordinary gas of sulphur, which is so dense that an equivalent is represented by only  $\frac{1}{6}$  of a volume, may not be the only one; that there may be, for example, a form in which half a volume, as in oxygen, or 1 volume, as in hydrogen, represents an equivalent? Oxygen is, in its ordinary state, of such a density that its equivalent occupies  $\frac{1}{2}$  a volume. But we now know that there exists an allotropic form of oxygen, not yet known in a state of purity, namely ozone, which is probably gaseous, and, if so, may have a different specific gravity. In practice, however, we cannot expect to reduce the equivalents of gaseous elements to equal volumes, because their usual forms often deviate from this, and we are compelled, therefore, to adopt the combining volumes already given.

#### ATOMIC OR EQUIVALENT VOLUMES.

The relation between the atomic weight and the specific gravity of bodies in the gaseous form has been briefly indicated in the preceding section. But the subject admits of being considered under different points of view, according to the notions entertained of the atomic constitution of gases. On the supposition, for example, that the atoms, or ultimate particles of all elementary gases, with their surrounding spheres of heat, possess the same volume, all such gases would contain, in equal volume, the same number of atoms. But as it is certain that compound gases do not, in all cases, contain the same number of atoms in equal volumes, it is quite possible that elementary gases may also differ in this respect; and, as above stated, the combining

volumes of sulphur and of some other elements agree with this conclusion. It is therefore generally admitted that equal volumes of different elementary gases contain different numbers of atoms; that, for example, 1 vol. of oxygen contains twice as many atoms, and 1 vol. of sulphur (in the form of gas) six times as many atoms, as 1 vol. of hydrogen, 1 vol. of nitrogen, or 1 vol. of chlorine. As above explained, this probably depends on the existence of allotropic modifications of these elements in the gaseous form, but for the present, we must take the fact as it is presented to us.

This obviously implies that the atoms, with their spheres of heat, are of different sizes; and, to take the cases above mentioned, that the atoms of oxygen gas are  $\frac{1}{2}$  the size, and those of sulphur  $\frac{1}{6}$  the size of the atoms of hydrogen, nitrogen, chlorine, &c. This is what is called the *atomic volume* of gases. It is not meant that we can ascertain the absolute volume of the atoms, but the relative or comparative volume of the atoms or particles of two or more gases.

Now, since the specific gravity of a gas depends on the number of atoms in a given volume, and on the weight of these atoms, it is evident that the atomic weight, divided by the specific gravity, must give the (relative) atomic volume.

For example, let hydrogen be taken as the standard for the specific gravity of gases, as it is for their atomic weights, then the atomic weight of hydrogen, = 1, divided by its specific gravity, = 1, will yield the quotient 1 for the atomic volume of hydrogen. Again, the atomic weight of oxygen, = 8, divided by its specific gravity, = 16 (that of hydrogen = 1), gives the quotient 0.5 or  $\frac{1}{2}$ , as the atomic volume of oxygen; and the atomic weight of sulphur, = 16, divided by its specific gravity as gas, = 96 (that of hydrogen = 1) gives the quotient 0.1666 or  $\frac{1}{6}$ , as the atomic volume of sulphur.

We thus see, that, on the supposition above adopted, that the atoms of different gases differ in size, we can prove that, whatever be the size of an atom of hydrogen gas, an atom of oxygen gas must be half, and that of an atom of sulphur gas one-sixth that size.

It is further obvious, that the number of atoms in equal volumes must be inversely as the atomic volume; or that the specific gravity of a gas, divided by its atomic weight, will give the number of atoms in a given volume. Hydrogen being retained as the standard, then we have  $\frac{1}{1} = 1$  = the number of atoms in 1 vol. of hydrogen: —  $\frac{16}{8} = 2$  = the number of atoms in 1 vol. of oxygen: and  $\frac{96}{16} = 6$  = the number of atoms in 1 vol. of gas of sulphur.

More briefly, the atomic volume and the number of atoms are the inverse of each other : so that we have  $\frac{1}{6}$  and 6,  $\frac{1}{2}$  and 2, 1 and 1.

If, while we make hydrogen the standard of atomic weights, we make air the standard of the specific gravity of gases, then we obtain, as quotients, a series of numbers equally comparable among themselves, but less simple and easy to retain than the above. We should have, for example,  $1 \div 0.0694 = 14.409$  for hydrogen ;  $8 \div 1.1057 = 7.2343$  for oxygen ; and  $16 \div 6.9000 = 2.3188$ , for sulphur ; and these numbers, which represent the atomic volumes, are to each other as 1,  $\frac{1}{2}$ , and  $\frac{1}{6}$ .

In the case of solids and liquids, the relation between atomic weight and specific gravity is far from being so simple, in consequence of the force of cohesion interfering with and disturbing the results. We cannot ascertain whether the atoms of solid bodies have the same size in different bodies, or not ; and we cannot tell whether the difference of specific gravity depends on a difference in the number of the atoms, in an equal volume, a difference in the size of the atoms, or a difference in the size of the interstices between the particles, or possibly on two or more of these causes.

Some chemists assume that there are no interstices, but that the atoms wholly fill up the space within the circumference of the body. On this supposition, the atomic weight, divided by the specific gravity (in solids and liquids), must give the atomic volume. It is difficult, however, to admit the absence of interstices, or pores in solids and liquids, if we consider them formed of atoms ; and it is perhaps better to use the term *equivalent volume*, instead of *atomic volume*.

The equivalent volume, then, of a solid or liquid is obtained by dividing the atomic weight (or rather equivalent number) by the specific gravity in the solid or liquid state. Water, the standard for the specific gravity of liquids, and solids, may be made the standard of equivalent volumes.

Thus the atomic weight of water, = 9, divided by its specific gravity = 1, gives the quotient 9 as its equivalent volume. The atomic weight of potassium, 39.26, divided by its specific gravity, 0.865, gives 45.387 for its equivalent volume ; and the atomic weight of carbon, 6, divided by its specific gravity in the form of diamond, = 3.5, the quotient 1.717 for the equivalent volume of the diamond.

On the other hand, the specific gravity, divided by the atomic weight, gives the relative number of atoms in a given volume, and in the case of potassium this is  $0.865 \div 39.26 = 0.0220$  ; in the case of carbon it is  $3.5 \div 6.04 = 0.5794$ . Finally, in the



case of water, the relative number of atoms in a given volume, which may be made the standard, is  $1 \div 9 = 0.1111$ . If, for convenience, the number for water is made 1000, then that for potassium becomes 198.0, and that for carbon becomes 5215.

Assuming, likewise for convenience, the equivalent volume of water (the standard) to be, (instead of 9) 1000, the equivalent volume of potassium becomes 5043, and that of carbon 191.666.

We thus perceive that the equivalent (or atomic) volume of carbon is about twenty-five times less than that of potassium, and that the number of atoms of carbon contained in a given volume is about twenty-five times greater than in the case of potassium. This compression of so large a number of atoms into a given volume may be the cause of the great hardness of the diamond.

The whole subject of equivalent volumes is full of interest : but as chemists have only recently begun to study solid and liquid bodies in this point of view, our knowledge on the subject is still very imperfect and limited. For what has lately been done, we are chiefly indebted to Kopp and to Schroeder.

Playfair and Joule have lately published the first part of an elaborate investigation concerning the volumes occupied by bodies both in the solid form and when dissolved in water ; and they have obtained results of an unexpected nature as well as of very great value.

The reader is referred to their paper in the *Memoirs of the Chemical Society*. Here we have only space to allude to the subject, and to mention that, among other curious results, these chemists have found that many salts, when dissolved in water, do not add to the bulk of the water more than is due to the water actually present in the salts. Thus for example alum, 1 eq. of which contains 23 equivalents of the elements potassium, aluminium, sulphur, and oxygen, besides 24 eq. of water, dissolves in water without increasing its bulk more than the addition of the 24 eq. of water must necessarily do ; so that the 23 eq. above-mentioned occupy no additional space, and must either be contained in the pores or interstices of the water, or disappear altogether as far as the occupying of space is concerned, if water be supposed to have no pores.

They have further shown that when salts do add to the bulk of the water in which they are dissolved, the increase of the bulk corresponds to that of a volume, or some multiple of a volume, of water. It is evident that these and similar researches must soon greatly extend our knowledge of the mechanical constitution of matter.

## ISOMORPHISM.

Most substances, when they assume the solid form slowly, so as to allow the particles to follow their natural attractions, exhibit, more or less perfectly, a regular form: in other words, they crystallise. Thus carbon, when slowly deposited in the form of diamond, assumes the form of a regular octohedron, or of some form geometrically allied to it; and common salt, a compound body, takes the form of the cube and its modifications, including the octohedron.

Now it has been observed that the same substance invariably crystallises in forms belonging to the same system, but that different substances very frequently present different crystalline forms. Thus, while diamond crystallises in regular octohedrons, iodine forms acute rhombic octohedrons: and while common salt crystallises in cubes, chloride of barium yields right rhombic prisms.

It happens occasionally, but rarely, that the same element is capable of assuming two crystalline forms, belonging to different systems, and not geometrically connected with each other. Thus sulphur, crystallising from its solution in bisulphuret of carbon, forms very acute rhombic octohedrons, but when melted by heat, and allowed to consolidate by cooling, it yields oblique rhombic prisms.

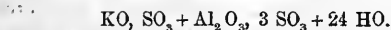
The same is occasionally observed in compound bodies. Thus carbonate of lime, in its common form of Iceland spar, crystallises in obtuse rhombohedrons and in innumerable varieties of that form: but in the rarer form of arragonite, it assumes the form of a rhombic prism.

These cases, and others which are analogous, are to be explained by a different arrangement of particles, dependent most probably on a difference of temperature at the period of the formation of the crystals. They are not, however, numerous enough to affect the general law, that the same substance always assumes the same crystalline form.

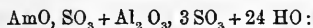
But the admirable researches of Gay-Lussac and of Mitscherlich have established the fact that, in many instances, different compounds assume the same form. Thus, the following substances, and many others, take the form of the cube, tetrahedron, or regular octohedron, which are geometrically connected. Chloride of sodium (sea-salt), chloride of potassium, sal-ammoniac, bromide of potassium, iodide of potassium, sulphuret of lead, fluoride of calcium, bisulphuret of iron, arseniuret of cobalt, sulphate of alumina and potash (alum), ammonia alun,

chrome alum, iron alum, sesquioxide of iron, sesquioxide of aluminium, sesquioxide of chromium. In like manner, other crystalline forms are found to be common to many different compounds, although none occurs so frequently as the cube and its congeners.

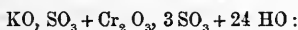
Now at first sight it would appear that no relation whatever could exist between the form of these numerous and very different compounds, and their composition. But on closer inspection, they are found to arrange themselves into groups. Of these groups, two may be specified among the compounds above enumerated. One is that of the chlorides, bromides, iodides, fluorides, and sulphurets of metals, having the formula  $MR$ , that is, 1 at. of metal to 1 at. of radical. This includes chloride of potassium  $KCl$ , of sodium  $NaCl$ , of ammonium (sal-ammoniac)  $AmCl$ ;\* to which may be added bromide of potassium  $KBr$ , iodide of potassium  $KI$ , fluoride of calcium  $CaF$ , and sulphuret of lead  $PbS$ ; and this group is a very large one. It will be observed that the members of it contain an equivalent of a metal united to 1 equivalent of a metalloid, and are therefore, so far, analogous in composition. The next group is that of the alums. Common alum has this formula,



Now if we substitute ammonium for potassium, we have



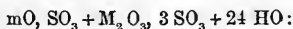
and this is the formula of ammonia alum. Chrome alum is



and another may be formed by substituting  $Am$  for  $K$ . Iron alum is



And here also another alum is obtained by substituting  $Am$  for  $K$ . A good many more alums may be procured by substituting  $Na$  (sodium) for  $K$ , and  $Mn$  for  $Al$ , that is, manganese for aluminium; and all these salts have the same crystalline form and the same general properties. Here, as in the former more simple group, the analogy in constitution is at once obvious. Every alum is



$m$  stands for a metal of one class, such as potassium, sodium or ammonium; and  $M$  for a metal of another class, such as aluminium, iron, chromium or manganese. It appears, therefore, that

\* See the section on Ammonium.

a salt, containing 1 eq. of a neutral sulphate of a protoxide of one of the former metals ( $\text{mO}$ ,  $\text{SO}_3$ ), along with 1 eq. of a neutral tersulphate of a sesquioxide of one of the latter metals ( $\text{M}_2\text{O}_3$ ,  $3\text{SO}_3$ ), and 24 eq. of water ( $24\text{HO}$ ) takes the crystalline form of common alum, the type of this group. From this we must conclude that the similar *arrangement* of particles prevailing in all these alums is one chief cause of the similarity in form. We see that the particles need not be all identical in two similar crystals; for example, of common alum and of iron alum. But there must be an analogy between those elements the equivalents of which may be mutually substituted for each other. We find accordingly, in all other relations, an analogy between potassium, sodium, and ammonium, on the one hand, and between aluminium, iron, chromium, and manganese on the other. In the group first mentioned, that of the chlorides, bromides, and iodides of certain metals, we find the same analogy between potassium, sodium, ammonium, calcium, and lead on the one side, and between chlorine, bromine, iodine, fluorine, and sulphur on the other.

Now to these groups of analogous elements, the name of isomorphous groups has been given, as there is every reason to believe that, as elements, they possess the same form (*ἴσος*, equal, and *μορφή*, form); and the phenomena of identical form in compounds of different but analogous composition, have received the name of isomorphism. Two elements are isomorphous, which either crystallise in the same form, or may be substituted for each other in their compounds, equivalent for equivalent, (the other elements remaining unchanged) without affecting the form of the compound.

The doctrine of isomorphism enables us, in many cases, to decide on the formula of a compound, and, consequently, on its equivalent. Thus, we have seen that aluminium or iron may be replaced by chromium, without change of form, in alum; and we find that sesquioxide of aluminium, sesquioxide of iron, and oxide of chromium, also crystallise in the same form. Now, the composition of oxide of chromium was formerly uncertain; but, finding as we do that it is isomorphous with the other two sesquioxides, we conclude that it is also a sesquioxide, and that its formula is  $\text{Cr}_2\text{O}_3$ .

Again, chromic acid is found to contain twice as much oxygen for the same amount of chromium, or it may be represented as  $\text{Cr}_2\text{O}_6$ . This being a most improbable formula, we observe next, that chromic acid may be substituted for sulphuric acid, without change of form; in other words, these acids are isomorphous. But the formula of sulphuric acid is  $\text{SO}_3$ , and we, therefore,

conclude, that the formula of chromic acid is  $\text{CrO}_3$ ; which agrees perfectly with the first observation, that it contains twice as much oxygen for the same weight of chromium as the oxide does; for  $\text{CrO}_3$  is the very same proportion as  $\text{Cr}_2\text{O}_6$ .

The following isomorphous groups have been established, and the existence of more is highly probable :—

|                        |                         |   |     |
|------------------------|-------------------------|---|-----|
| 1.                     |                         | 7.  |     |
| Silver . . . .         | Ag                      | Salts of potash . . .                     | KO  |
| Gold . . . . .         | Au                      | Salts of oxide of ammo-                   |     |
|                        |                         | nium . . . . .                            | AmO |
| 2.                     |                         | (Or ammonia $\text{N H}_3$ +              |     |
| Arsenious Acid (in its |                         | water, $\text{HO}=\text{NH}_4\text{O}$ ). |     |
| unusual form) . .      | $\text{AsO}_3$          |   |     |
| Teroxide of Antimony   | $\text{SbO}_3$          | 8.  |     |
|                        |                         | Oxide of silver . . .                     | AgO |
| 3.                     |                         | Oxide of sodium . . .                     | NaO |
| Alumina . . . .        | $\text{Al}_2\text{O}_3$ | 9.  |     |
| Sesquioxide of iron .  | $\text{Fe}_2\text{O}_3$ | Baryta . . . . .                          | BaO |
| „ chromium . . .       | $\text{Cr}_2\text{O}_3$ | Strontia . . . . .                        | SrO |
| „ manganese . .        | $\text{Mn}_2\text{O}_3$ | Lime (in arragonite) .                    | CaO |
|                        |                         | Oxide of lead . . . .                     | PbO |
| 4.                     |                         | 10.                                       |     |
| Phosphoric acid . .    | $\text{PO}_5$           | Lime (in Iceland spar) .                  | CaO |
| Arsenic acid . . .     | $\text{AsO}_5$          | Magnesia . . . . .                        | MgO |
| 5.                     |                         | Protoxide of iron . .                     | FeO |
| Sulphuric acid . . .   | $\text{SO}_3$           | „ manganese . . . .                       | MnO |
| Selenic acid . . . .   | $\text{SeO}_3$          | „ zinc . . . . .                          | ZnO |
| Chromic acid . . . .   | $\text{CrO}_3$          | „ cobalt . . . . .                        | CoO |
| Manganic acid . . .    | $\text{MnO}_3$          | „ nickel . . . . .                        | NiO |
|                        |                         | „ copper . . . . .                        | CuO |
| 6.                     |                         | „ lead (in                                |     |
| Hypermanganic acid .   | $\text{Mn}_2\text{O}_7$ | plumbo-calcite) .                         | PbO |
| Hyperchloric acid .    | $\text{ClO}_7$          |   |     |

The above groups are almost all formed of compounds; either because these compounds are found to be actually isomorphous when themselves crystallised, as, for example, the sesquioxides in group 3; or because they may be mutually substituted for each other, in those compounds into which they enter, without change of form. This, as we have seen, is the case with the sesquioxides in the alums; and, indeed, three of these oxides have been obtained in crystals, and found to be themselves isomorphous. But it is also the case with the acids; for example, in groups 4 and 5, although we do not positively know, what is however most probable, that these acids possess, in each group respectively, the same form. Although, for example, we cannot say that arsenic and phosphoric acids are themselves isomorphous, since they do not crystallise, yet their salts are strictly isomor-

phous; and the analogy extends not only to form, but to colour, taste, and many other external qualities. So strong, indeed, is this external resemblance that, in many cases, we must actually decompose one of these salts, and ascertain whether it contain arsenic or phosphorus, before we can say whether the salt is an arseniate or a phosphate. The same extraordinary similarity in all external characters, is seen in the salts of the sulphuric and selenic acids.

We can hardly doubt that not only the salts, but the acids, are really isomorphous, and would be found so, if we could obtain them all in crystals; and we have the same reason to conclude that the elements of these acids are also isomorphous; that arsenic and phosphorus, sulphur and selenium, for example, crystallise, respectively, in the same form.

Indeed, the only plausible explanation of the existence of isomorphous groups of compounds is, that the elements characterising those groups are isomorphous, and that hence their analogous compounds are so. If we assume that arsenic and phosphorus are isomorphous, then we see that  $\text{AsO}_3$  must be isomorphous with  $\text{PO}_3$ , since the oxygen in both is, of course, the same. In like manner, arseniate of soda,  $\text{AsO}_3, 2\text{NaO}, \text{HO}, 24 \text{ aq.}$ , must be isomorphous with phosphate of soda,  $\text{PO}_3, 2 \text{ NaO}, \text{HO}, 24 \text{ aq.}$ , since all the elements in these two salts are the same in nature, number, and arrangement, except that As in the first is replaced by P in the second; and the elements As and P have been assumed to possess the same form.

There is one case which requires explanation. It is the isomorphism of potash,  $\text{KO}$ , and oxide of ammonium  $\text{NH}_4\text{O}$ ; or, in other words, ammonia with 1 at. of water,  $\text{NH}_3, \text{HO}$ . Here we have a body composed of 6 equivalents isomorphous with one containing only two. But, on the one hand, there is good reason to believe that the compound metal, ammonium,  $\text{NH}_4$ , exists; and if we represent this by a single symbol Am, its oxide will be  $\text{AmO}$ , corresponding in constitution to  $\text{KO}$ , each being formed of 1 eq. of metal and 1 eq. of oxygen. It is true Am is a compound; but, on the other hand, this compound acts as an element, and  $\text{Am} = \text{NH}_4$  is only 1 eq. of metal. Besides, we cannot be certain that even potassium, K, is not also a compound, although we have not as yet succeeded in decomposing it, if it be one. At all events, it is a fact, that  $\text{NH}_4$  may be substituted for K without affecting the form of the compound in which the substitution is made, as in the alums; and we have only to assume that the compound  $\text{NH}_4$  happens to be isomorphous with the simple substance K, and all the facts would follow.

We shall have occasion to return to the subject of isomorphism when treating of salts generally, and of their crystallisation.

It has been observed, that many substances, usually considered isomorphous, are not absolutely so ; that there is a certain amount of difference in the angles of the crystals, which, however, does not extend far. It is not precisely known what is the true cause of this phenomenon ; whether it depend on a small, but essential difference in the angles of the isomorphous elements ; or whether the same form may not, under certain circumstances, exhibit at one time, angles somewhat greater or less than at another. It is possible, for example, that the temperature at which the crystals were formed, or the presence of some impurity, may thus affect the crystalline forms. The phenomenon is called Plesiomorphism.

#### ISOMERISM.

We have seen that, as a general rule, analogy of composition implies analogy or similarity in form and external properties. But it has been observed in a number of cases, that two or more compounds, formed of the same elements, in the same relative proportions, and having, therefore, the same composition in 100 parts, are yet entirely distinct from each other in all their properties. Such bodies are called isomeric bodies (from *ἴσος*, equal, and *μέρος*, part).

It is obvious that, as the proportions of the elements are the same, the source of the difference in properties must be sought for in the *absolute number*, or in the *arrangement* of the atoms. Thus acetic ether and aldehyde are two entirely different liquids, containing exactly the same relative proportions of carbon, hydrogen, and oxygen. These proportions, reduced to the smallest number of atoms, are  $C_2H_2O$ . Now, there is no doubt that the absolute numbers in aldehyde are  $C_4H_4O_2$  ; and there is also no doubt that the absolute number of equivalents in acetic ether is  $C_8H_8O_4$ . Here it is evident that, although the proportions are the same, the equivalent of acetic ether is twice as large as the equivalent of aldehyde. Again, the composition, in 100 parts, and consequently the relative proportions of the elements, of urea is exactly the same as in hydrated cyanate of ammonia ; while the equivalent of both compounds appears to be the same, or, in other words, they contain the same absolute number of atoms of the element. But we know that the hydrated cyanate of ammonia is represented by  $NH_3 + C_2NO$ ,  $HO$  ; and that urea contains neither ammonia  $NH_3$ , nor cyanic acid

$C_2NO$ . Let us suppose the atoms in urea to be simply united thus,  $C_2N_2H_4O_2$ , and we see at once that the same relative and absolute number of atoms may readily give rise to perfectly distinct compounds. In some cases, we know what the arrangement is in both compounds. Thus, hydrated acetic acid,  $C_4H_8O_3$ ,  $HO$ , and formiate of oxide of methyle,  $C_2H_3O + C_2HO_3$ , both contain  $C_4H_4O_4$ . Such isomeric compounds are called *metameric*; and where the absolute number of atoms differs, *polymeric*; where the absolute number in one or both is unknown, they are called simply *isomeric*.

It is easy to see that, wherever the atoms of the elements of a compound admit of more than one arrangement, metameric compounds may occur. In binary compounds, such as water,  $HO$ , there is but one arrangement possible, as long as the absolute number of atoms is not doubled, trebled, or still further multiplied. But in such a compound as peroxide of iron,  $Fe_2O_3$ , for example, the elements might yield several metameric compounds, such as  $2FeO + O$ ,  $FeO + FeO_2$ ,  $Fe + FeO_3$ , not to mention the multitude of compounds which might be formed with precisely the same composition in 100 parts, by increasing the absolute number of atoms.

The discovery of isomerism, however unexpected, is thus entirely consistent with the atomic theory, of which it is merely a special case. Isomerism, though rare in inorganic chemistry, is of very frequent occurrence among organic compounds, owing, no doubt, to their usually large atomic weights, since the numerous atoms of the elements afford much scope for isomeric modifications; and doubtless this principle plays an important part in the processes of organic life and growth, as well as in decay.

#### ALLOTROPISM.

It has been already noticed (p. 42) that sulphur is capable of crystallising in two distinct and incompatible forms. These are now called different *allotropic* modifications of that element, from Greek words signifying "to turn another way," because the position of the molecules is necessarily different. This remarkable fact is not confined to the above example, for sulphur exists in a third allotropic modification, in which it is brown, viscid, and amorphous; and is moreover stated by Magnus to exist in two more allotropic forms, one black, the other red. Moreover, other elements exhibit similar phenomena. Carbon occurs in three allotropic forms; the diamond, which crystallises in octohedrons and is transparent; graphite, which is opaque, black, and crystallised in prisms; and common



charcoal, lamp-black, &c., which are black and quite amorphous. Phosphorus also occurs in two allotropic forms; the ordinary one, which crystallises and is white and translucent, and readily inflammable; and the new form, which is deep reddish-brown, amorphous, more dense, and very much less easily inflammable. It is also said to yield several other allotropic modifications. Now, sulphur, carbon, and phosphorus, are elementary bodies, and yet assume appearances as distinct as if they were different bodies; for diamond and lamp-black, yellow crystallised sulphur and brown plastic sulphur, white and red phosphorus, are respectively quite different in physical characters. Various metals exhibit analogous phenomena; we have gold as a yellow metal, and as a brown powder; also as a black powder; platinum as a white metal, and as a black powder, &c. The allotropic forms of sulphur are probably traceable in the different liquid states in which it occurs: the same is probably true of phosphorus; and in the case of oxygen, we see that an element may assume two different gaseous states. Ordinary oxygen is devoid of smell, and acts slowly, or not at all, on many bodies at the ordinary temperature. It is called the passive form. But ozone, the active form of oxygen, has so intense an odour, somewhat like that of chlorine, that a mere trace of it gives to air a very pungent smell; and it instantly acts on almost all oxidisable bodies. It has been proved, that ozone contains nothing but oxygen, and that by a very moderate heat, the active is converted into the passive form. Such differences in elementary bodies can only be explained by supposing the ultimate atoms to be differently grouped to form the actual molecules, for example, of diamond and of lamp-black; or else by supposing that the molecules, in one allotropic form, contain a larger or a smaller number of ultimate atoms. Or it is possible that both causes may combine to produce the result. The difference in the crystalline form of the two crystallised forms of carbon and of sulphur, respectively indicate a difference in the position or arrangement of the molecules; but these may also differ in the number of ultimate atoms they contain, and may thus acquire different forms. The allotropic modifications of the same element differ also in density, and there is some reason to think that in sulphur at least, the allotropic differences persist in the liquid and gaseous states.

The different allotropic forms of the elements are often distinguished by subjoining Greek letters. Thus the natural crystals of sulphur, which are rhombic octahedrons, are  $S_{\alpha}$ , the artificial prismatic crystals are  $S_{\beta}$ , and the viscid form is  $S_{\gamma}$ . Passive oxygen will be  $O_{\alpha}$ , and active oxygen, or ozone,  $O_{\beta}$ , &c.

The occurrences of such marked differences in the properties of elementary bodies is very remarkable, and of great interest in reference to the molecular constitution of matter, but the subject has not yet been fully investigated.

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Having premised the preceding general or introductory remarks, we now proceed to the actual description of the element, and of their compounds, which constitutes chemistry, properly so called.

It is not possible, in the present state of our knowledge, to follow any arrangement that shall not be open to objection. The different classes or groups of elements are not so clearly characterised as to permit us to follow a strictly scientific arrangement, and therefore we shall only adhere to the division of the elements into metalloids and metals ; and, beginning with the former, describe the elements in the order of their importance and interest. It has already been stated, that even this division is not always fully observable, since selenium is classed by some as a metal, and arsenic by others as a metalloid.

## METALLOIDS.

THERE can be no hesitation as to that element which, being the most important of all, ought to be first treated. We therefore proceed to describe—

1. OXYGEN.  $O = 8$ .

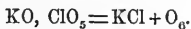
which is of all elements the most abundant ; forms 89 p. c. by weight of all the water, and 23 p. c. of the atmospheric air of our globe : exists in all rocks, except rock salt ; and is an essential element in all animal and vegetable bodies. It constitutes at least  $\frac{1}{3}$  of the weight of our earth.

Obtained most easily by applying a heat rather below redness to a mixture of chlorate of potash with  $\frac{1}{2}$  of its weight of peroxide of manganese.

The latter undergoes no change, but promotes in a high degree the decomposition of the chlorate. The

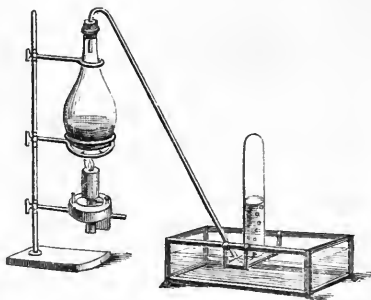
mixture being introduced into a small retort, or a small flask with a bent tube, may be heated by a spirit lamp, and the gas which comes off very

abundantly and rapidly, collected over water, in the pneumatic trough. The chemical change caused in the chlorate by heat is represented as follows :



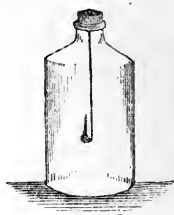
That is, 1 eq. of the salt yields 1 eq. of chloride of potassium, KCl, which remains in the retort, and 6 eq. of oxygen, which escape in the form of gas.

*Properties.*—A gas, colourless, tasteless, inodorous. Specific gravity (air = 1.000) according to Thomson, 1.1111, but, by the most recent researches, 1.1057. 100 cubic inches of it weighed 34.203 grains. A burning body, as a match of wood or paper, burns in the gas with greatly increased brilliancy ; a spark on a piece of wood bursts out into flame. Iron wire burns



in it, when heated white hot, with beautiful sparks. This is managed, by attaching to the end of the wire a little German tinder or sulphur, setting fire to this, and then introducing the coil of wire into oxygen. The point is thus heated to the requisite degree, and when once begun, the combustion of the wire continues till all the oxygen is consumed. Phosphorus, if already burning, or when touched with a hot wire, burns in it with an intensely dazzling white light, &c.

Oxygen combines with all the other elements (except perhaps fluorine), and with most of them in several proportions. The combustion of bodies in oxygen is nothing but their combination with that element; the process, from the energy of the affinities, being attended with heat and light. Thus, when iron



burns in oxygen, it yields oxide of iron  $\text{FeO}$ ; and when phosphorus burns in oxygen, it produces phosphoric acid,  $\text{PO}_5$ . In all such cases, the oxygen and the combustible body disappear, and a new compound results.

Combustion, or the combination of a combustible with oxygen, goes on in atmospheric air, but much less rapidly and vividly than in pure oxygen, because in air, the oxygen is diluted with four times its bulk of nitrogen.

Many substances slowly combine with oxygen without the manifestation of heat or light; as for example, iron, when it rusts.

In every case the combustible is said to be oxidised, or to undergo oxidation, and the compound formed is termed an oxide.

The whole structure of modern Chemistry is founded on the above simple theory of combustion, first proposed by Lavoisier; who, by using the balance, discovered that the burning body became heavier during the process, and could not, therefore, according to the then prevalent theory, have lost phlogiston (an imaginary element), or anything else.

Lavoisier having observed that all the acids then known were compounds of oxygen with combustible bodies, concluded

that acidity depended on the presence of oxygen, and named that element accordingly (from *οξύς*, acid, and *γεννάω*, to produce). The name is still retained, although we are now acquainted with many acids which contain no oxygen; and although, according to views now considered probable, hydrogen has more claim to the title of the producer of acids than oxygen. Besides, oxygen is now known to be an essential ingredient in bases, the basic power of which really seems to be in a close relation to their amount of oxygen. But the inconvenience of changing the name would be very great, so that while many of the views of Lavoisier have been abandoned, his names are retained.

Lavoisier, among other views, held that combustion could not take place without the presence of oxygen. But subsequent experience has shown that although all combustions in our atmosphere, or in oxygen gas, depend on the presence of oxygen; the phenomenon of combustion is nothing more or less than chemical combination, attended by heat and light. Many examples might be adduced of combustion without oxygen; take, for example, the case of iron and sulphur, which, when heated, combine with much heat and light; or that of phosphorus, which when introduced into chlorine, takes fire and burns, combining with the gas. Although, therefore, oxygen is concerned in all ordinary combustions, that is, in all which take place in our atmosphere, the student must bear in mind the true definition of combustion;—namely, “chemical combination, attended with heat and light.”

Oxygen has been termed a supporter of combustion, as distinguished from a combustible body, such as phosphorus. But we are not to suppose that the oxygen has any greater, or any other share in combustion, than the phosphorus. It so happens, that the oxygen is a gas, and the phosphorus a solid. The heat and light, therefore, appear to proceed from the phosphorus; because the combustion can only take place where the two bodies are in contact. But, in reality, both bodies are equally concerned in the production of the heat and light; and while we may call phosphorus a supporter of combustion as well as oxygen, we may call oxygen a combustible as well as phosphorus.

In all combustions in our atmosphere, the heat and light, as above explained, although derived equally from both bodies, or rather, from the process of combination, appear to proceed from what is usually called the combustible or burning body, because it is usually solid or liquid, or if a gas, issues from a jet, and is surrounded by an atmosphere containing oxygen, which can only

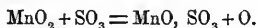
act on the combustile at the surface of the latter. But this is merely appearance ; for while a jet of hydrogen, set fire to in a jar of oxygen, seems to burn and to give out the heat and light, a jet of oxygen in a jar of hydrogen may be set fire to and will then appear, as the hydrogen did before, to be the source of the heat and light, which in both cases was derived from the combination of oxygen with hydrogen.

These principles are farther illustrated by the mode in which phosphorus burns in oxygen gas. When the phosphorus is heated, it first melts, then takes fire, and for some time the heat and light appear, as usual, to proceed from the phosphorus. But as the temperature rises rapidly, it reaches at last the boiling point of that element, when the phosphorus spreads as vapour or gas throughout the oxygen, combination takes place at all points, and the whole vessel is filled with a dazzling light, which is as bright at the circumference as at the centre. When only a small quantity of phosphorus is used, this splendid appearance is not seen, because when the heat rises to the boiling point, all the phosphorus is already consumed.

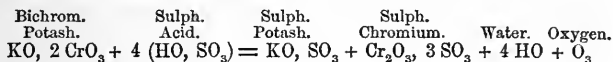
Another beautiful experiment serves to show oxygen in the light of a combustile body, and coal gas in that of a supporter of combustion. A mixture of chlorate of potash and peroxide of manganese is heated in a platinum crucible, supported on a bent wire, by the flame of a spirit lamp, till it begins to give off oxygen rapidly. At this moment a light is applied to the aperture of a jar full of coal gas, this aperture being only just wide enough to admit the crucible. The gas takes fire, and the crucible, heated as above, is rapidly introduced through the flame (which is extinguished by a metallic plate fixed at a proper height on the wire, so as to shut the aperture) into the jar. In passing through the flame, the oxygen takes fire, and as the heat causes the oxygen to escape very rapidly, it burns quickly out, with a kind of flash, filling the jar with a fine pinkish white flame. If the crucible be less strongly heated at first, the oxygen will often burn in a short pink flame rising from the crucible for some time, but generally flashes up at the end. This experiment clearly shows the real nature of combustion, and it is evident, that if our atmosphere consisted of coal gas, we should have to search, not for coal to burn in it, but for substances capable of yielding oxygen, such as oxide of manganese, nitre, or chlorate of potash.

Oxygen is necessary to the respiration of animals : but for this purpose pure oxygen is not fitted ; and it has, therefore, in our atmosphere been diluted with four times its volume of another gas.

When a large quantity of oxygen gas is required, it is generally prepared by heating to redness, in an iron bottle, the peroxide of manganese, of which 3 eq. are believed to yield 2 eq. of oxygen according to the equation  $3 \text{ MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$ . The oxygen thus obtained is one third of that contained in the oxide. The residue  $\text{Mn}_3\text{O}_4$  is a compound of the protoxide and sesquioxide,  $\text{MnO} + \text{Mn}_2\text{O}_3$ , and is called the red oxide. Oxygen may also be obtained by the action of heat on nitrate of potash or nitre, on red oxide of mercury, or on red oxide of lead. In practice, the chlorate of potash (of which 124 parts yield 48 of very pure oxygen), although rather a dear salt, and the peroxide of manganese, which, although not very productive, is very cheap, are alone employed. On the small scale, the peroxide of manganese, heated with sulphuric acid, yields considerably more oxygen than when heated *per se*, according to the equation :

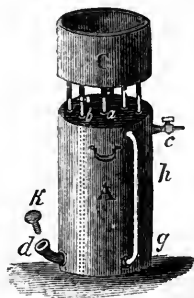


The sulphate of protoxide of manganese,  $\text{MnO}, \text{SO}_3$ , remains in the retort. This process is troublesome, and the retort is generally broken during cooling. A better process, lately proposed, is to heat bichromate of potash with an excess of sulphuric acid. This process is explained by the following equation :



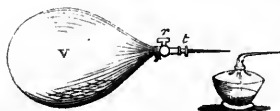
The residue, if properly treated, may be made to yield chrome alum  $\text{KO}, \text{SO}_3 + \text{Cr}_2\text{O}_3, 3\text{SO}_3 + 24\text{HO}$ ; a salt which forms large octohedral crystals, black by reflected, purple by transmitted light, and green when reduced to powder.

Large quantities of oxygen are conveniently collected in the gas-holder of Pepys, the construction of which is shown in the figure. The aperture *d* being closed, and the stopcocks *b* and *c* above being opened, water is poured into the trough *C*, which water descends by the long tube *b*, and expels the air by the stopcock *c*. When all the air is expelled, the upper stopcocks are all closed, and the plug removed from *d*, out of which no water flows, because the short tube points upwards, and the external air cannot ascend through it to displace the water. The gas tube is now introduced at *d*, and as the gas rises, the water flows out at *d*.



till the gas-holder is full, when *d* is closed. When the gas is wanted, water is poured into *C* as at first, the stopcock *b* is opened, to allow the water to press on the gas, which will then escape either by the stopcock *c* or by the middle one *a*, if these or one of them be opened, and may be collected over *a* in *C*, or conveyed by a tube from *c* to any vessel we desire to fill with it.

If we desire to obtain, on a small scale, a very intense heat, we may either cause a current of oxygen from the gas-holder to



play through a blow-pipe tube on the flame of a spirit-lamp ; or we may fill a bladder with oxygen from the gas-holder, or from a tubulated bell-jar, and force the gas through a tube

into the flame of the lamp, as in the figure. The heat thus produced will readily burn iron or steel, and melt platinum.

Since oxygen unites with all the other elements, and forms very numerous and important compounds, it may be well here to mention the principal classes of oxidised bodies, or oxides, as the compounds of oxygen are called.

The most numerous class of oxides is that of the basic oxides, or bases. These are formed, in every case, by the union of a metal with oxygen. The most frequent formula for a basic oxide is  $MO$  (*M* representing 1 eq. of a metal). Examples, potash  $KO$ , lime  $CaO$ , protoxide of iron  $FeO$ , protoxide of manganese  $MnO$ . Such bases are called protoxides. Next to these in importance are the sesquioxides, the formula of which is  $M_2O_3$ . Examples, sesquioxide of iron  $Fe_2O_3$ , sesquioxide of manganese  $Mn_2O_3$ , sesquioxide of aluminium  $Al_2O_3$ . Sesquioxides are in all cases weaker bases than the protoxides of the same metals ; and, generally speaking, they are found to be weaker bases than protoxides. Oxides of the formula  $MO_2$  are either neutral, as peroxide of manganese  $MnO_2$ , and superoxide of lead  $PbO_2$  ; or weak acids, such as stannic acid  $SnO_2$ . But there are a very few basic oxides of the formula  $M_2O$ . Example, suboxide of copper  $Cu_2O$ . These bases are very feeble, compared to the preceding kinds.

The next important class of oxides is that of the oxygen acids. These are most frequently composed of metalloids united to oxygen ; but there are also oxygen acids formed of metals united to oxygen. Examples of the former, carbonic acid  $CO_2$ , sulphuric acid  $SO_3$ , phosphorous acid  $PO_3$ , phosphoric acid  $PO_5$ , nitric acid  $NO_5$ , hyperchloric acid  $ClO_7$  : of the latter, stannic acid  $SnO_2$ , already mentioned, arsenious acid  $AsO_3$ , chromic acid  $CrO_3$ , manganic acid  $MnO_3$ , hypermanganic acid  $Mn_2O_7$ .



It will be observed that the formulæ of acids are very various ; and it will also be noticed that where a metal forms an acid with oxygen, that acid contains more oxygen than the basic oxide or oxides of the same metal. Thus, protoxide of manganese, which is a strong base, is  $\text{MnO}$ , while manganese yields two acids, manganic acid  $\text{MnO}_3$ , and hypermanganic acid  $\text{Mn}_2\text{O}_7$ .

The third class of oxides is that of the neutral or indifferent oxides. These are neither decidedly acid, nor decidedly basic, and some of them play both parts ; on the one hand combining with bases, as a weak acid would do ; on the other, uniting with acids like a weak base. This is the case with water,  $\text{HO}$ , which, itself neutral, combines both with acids and bases, forming compounds which are still acid or basic, and are called hydrates. Examples,  $\text{HO}$ ,  $\text{SO}_3$ , oil of vitriol, or hydrated sulphuric acid ;  $\text{KO}$ ,  $\text{HO}$ , caustic potash, or hydrate of potash. Water also combines with neutral salts, as in protosulphate of iron dried at a moderate heat,  $\text{FeO}$ ,  $\text{SO}_3$ ,  $\text{HO}$ . In this, and many other salts water further plays a fourth part, that of water of crystallisation, which is often distinguished from acid, basic, or saline water, by being written thus ; aq. The crystals of protosulphate of iron are  $\text{FeO}$ ,  $\text{SO}_3$ ,  $\text{HO} + 6 \text{ aq.}$  ; and in such salts the saline atom of water requires a much stronger heat to expel it than the atoms of water of crystallisation. Others do not enter into any combination, but are strictly indifferent ; such as deutoxide of hydrogen  $\text{HO}_2$ , and deutoxide (binoxide, peroxide, or superoxide) of manganese,  $\text{MnO}_2$ , or of lead,  $\text{PbO}_2$ . Where, as in the case of manganese, the metal also forms a basic oxide or oxides, and an acid or acids, it is important to notice, that the indifferent oxide is intermediate in composition, as if a certain proportion of oxygen communicated basic properties, a somewhat larger proportion destroyed these without producing acidity, and a still larger share of oxygen gave to the compound distinctly acid characters. By inspecting the compounds of manganese with oxygen, we further see that of the two basic oxides, both of which contain less oxygen than the indifferent oxide, or superoxide, that which contains the most oxygen is the weaker base.

$\text{MnO}$  Protoxide of manganese.

$\text{Mn}_2\text{O}_3$  Sesquioxide of do.

$\text{MnO}_2$  Superoxide of do.

$\text{MnO}_3$  Manganic acid.

$\text{Mn}_2\text{O}_7$  Hypermanganic acid.

A powerful base.

A feeble base.

Neither basic nor acid.

A strong acid.

A strong acid.

When the superoxide, or indifferent oxide of a metal, is acted on by an acid it loses oxygen, while a basic oxide, being left,

combines with the acid ; as in the process for obtaining oxygen by the action of sulphuric acid on peroxide of manganese, given and explained at p. 55.

Oxygen was discovered by Priestley, in 1774 : and in the following year by the Swedish chemist Scheele, without any knowledge of Priestley's discovery. The time, in fact, had come when chemistry was studied in the true scientific spirit ; and had these illustrious men not then discovered oxygen, it must, nevertheless, have been very soon discovered by some one else.

The chief uses of oxygen have been already alluded to. As it occurs in the atmosphere it is essential to respiration, to all ordinary processes of combustion, and also to another process of the greatest importance, namely, to the decay of dead plants and animals, which is, in fact, a slow combustion, unattended with light, and has been named "eremacausis." That it is not unattended with heat is proved by the occurrence of spontaneous combustion in certain substances when exposed to air. We shall return to this subject when treating of the atmosphere, in which, and not in pure oxygen, eremacausis and spontaneous combustion occur.

Oxygen has of late years been used to produce an intense light, which is obtained by supplying to burning naphtha, camphine, or oil of turpentine, a current of the gas.

Of all the elements, oxygen is the most abundant, forming, as already mentioned,  $\frac{8}{10}$  of all the water on our planet,  $\frac{1}{5}$  of all the atmosphere, and a large proportion of all rocks and earths, except rock-salt, besides being an essential ingredient of all organised bodies, animal or vegetable, even when dried so as to expel all the water they contain, which, on an average, is little less than  $\frac{2}{3}$  of the weight of the living plants and animals. Yet although it is so very abundant, and in the atmosphere is only mixed, not chemically combined, with nitrogen, it is not easy to procure oxygen in a pure state in large quantities, nor can this be done cheaply. This arises from the very strong affinities of oxygen ; and the only substances which readily yield it are compounds containing an excess of oxygen, part of which, or in some cases the whole, may be expelled by heat. No method is known by which the nitrogen of atmospheric air can be removed, so as to leave the oxygen, although we have many ways of absorbing the oxygen and leaving the nitrogen. Perhaps the power of the electric current to decompose water, separating the oxygen and hydrogen, may some day be so used as to supply oxygen *ad libitum* ; and this is the more desirable, because water is

not only most abundant, but contains more oxygen than any other compound. At present, however, an electric current of such force as to decompose water rapidly, can only be supplied at an expense which forbids its use for this purpose. But we have seen such extraordinary progress made in electricity, that we may hope some day to see it applied cheaply in this way. Perhaps means may be found to collect and apply the electric currents of the earth or of the atmosphere.

*Ozone.* The oxygen above described is  $O_a$ , the first or passive allotropic form of that element. The second, or active form,  $O_b$ , usually called ozone, is a still more remarkable substance, which was discovered some years since by Schönbein, although its true nature has only recently been ascertained.

It had been long observed that the oxygen formed in the decomposition of water by the electric current, under certain conditions, exhaled a peculiar pungent odour. Schönbein investigated the subject with great industry and patience, and found that this odour was due to the presence of a minute quantity of a new substance, which he named ozone, from its strong smell. He showed that it is formed also under other circumstances, as when electric sparks are passed through dry oxygen in a tube ; when sticks of phosphorus are placed in the bottom of large bottles containing air, and are half covered with water. He also pointed out that the peculiar smell, often perceived during thunderstorms, is that of ozone.

In whichever of the methods above indicated, ozone is prepared, it is never formed but in very minute proportion, and it is not yet known in a pure state. Our experiments can only be made therefore with air or oxygen containing a trace of ozone. If we seek to increase its amount by the electric spark, it is decomposed ; if we leave it long in contact with the phosphorus in the other process, it is absorbed by the phosphorus.

But even in the very diluted state in which only it is known to us, ozone is the most energetic oxidising agent known. It rapidly corrodes metals—iron and copper for example—and even such as silver, if moist, the silver forming a peroxide. It corrodes with equal power the most indifferent organic substances, such as caoutchouc or cork. It rapidly oxidises the black sulphuret of lead, if moist, into the white sulphate. Paper, moistened with sulphate of manganese, is turned brown by it, the manganese being peroxidised. All iodides are instantly decomposed, the iodine being set free, and iodine itself is oxidised by ozone into iodic acid. It also bleaches organic colours strongly. None of these effects can be produced by passive oxygen.

The easiest and best method of detecting ozone is to use paper which has been steeped in a weak solution of iodide of potassium containing starch, and then dried and kept in well closed vessels. For use, the paper is moistened and exposed to the gas supposed to contain ozone, when, if ozone be present, even in minute proportion, the paper is turned blue. In this way we can detect ozone in a few minutes after phosphorus has been exposed to air in a bottle, as above described ; and in this way Schönbein was able to detect it in the atmosphere, not only during thunderstorms, but very often at other times. He found that in storms when the electric discharge took place at a great distance from where he was, he could often instantly detect ozone, although within four walls, and although previously the paper was quite unaffected.

It is evident that ozone cannot accumulate in the air, because it instantly oxidises all oxidisable gases or vapours, as well as all dead organic matter, in the atmosphere or on the earth's surface, and is therefore consumed as fast as it is produced. It is probably well for us that pure or concentrated ozone, for this reason, cannot occur in the air, for it would burn up not only dead but living animals and plants.

Ozone may be recognised by its smell, which has some analogy with that of chlorine, though quite peculiar. It is re-converted into passive oxygen, not only by a continuance of electric sparks, but also by a heat not much beyond that of boiling water. If the air of a jar, charged with ozone, be made to pass through a tube, part of which is heated by a spirit lamp, the gas as it issues from the tube, no longer affects the test paper.

It was at one time supposed that ozone contained hydrogen, and it has been described as an oxide of hydrogen  $\text{HO}_3$ . But even when formed in contact with water, there appears to be but one ozone, and that  $\text{O}_3$ . The recent researches of Andrews seem to establish this point beyond doubt, and it is certain that perfectly dry oxygen yields ozone when electric sparks are passed through it.

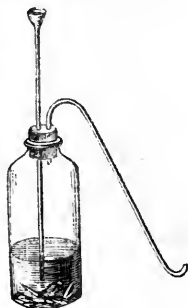
## 2. HYDROGEN. $\text{H} = 1$ .

Occurs in nature only in combination, chiefly in the form of water, of which it constitutes 11 per cent. by weight. It is an essential ingredient in all organised bodies.

It may be easily prepared by causing diluted sulphuric or hydrochloric acid to act on iron filings, or on granulated zinc. The best apparatus for the purpose is a wide-mouthed bottle, furnished with a closely-fitting cork. In this cork are made two

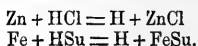
holes, into one of which, a tube properly bent is closely fitted, while into the other is inserted, also air-tight, a straight tube reaching to the bottom of the bottle, and widened at its upper end, so as to form a funnel. Both tubes are open at both ends, and the bent tube terminates, within the bottle, just below the cork, while its further end dips under water in the pneumatic trough.

The metal being introduced into the bottle, and covered to the depth of an inch by water, the cork with the tubes is fitted in : the acid is poured in through the straight tube, and the bottle shaken, so as to mix the acid and water thoroughly. Enough of acid should be added to cause a brisk, but not violent effervescence, and as the end of the straight tube is covered by the liquid, the gas produced can only escape through the bent tube. Care must be taken not to collect the gas for use until the whole of the air originally in the upper part of the bottle has been expelled ; otherwise the application of a light might cause a dangerous explosion. Perhaps the safest way is to collect, in a large jar full of water, as much of the gas which first escapes as would suffice to fill the gas-bottle twice, and to throw this away : what comes subsequently is pure. When the current of gas slackens, the addition of a little more acid, through the straight tube, causes it again to go on as briskly as at first.



When zinc and hydrochloric acid are employed, the process is represented by the following equation :  $\text{Zn} + \text{HCl} = \text{H} + \text{ZnCl}$ . That is, the zinc takes the chlorine of the acid, forming chloride of zinc, and the hydrogen is separated. When iron and sulphuric acid are used, the process is expressed by the equation  $\text{Fe} + \text{HO}, \text{SO}_3 = \text{H} + \text{FeO}, \text{SO}_3$ . Here the hydrogen is supposed to proceed from water, the oxygen of which forms, with the iron, protoxide of iron, which again unites with the sulphuric acid, forming sulphate of protoxide of iron. It is to be observed that this, the generally received explanation of the latter process, is very different from that of the former, although the phenomena in both are the same, namely, the escape of hydrogen and the formation of a neutral salt. But we have only to modify the formulæ of sulphuric acid and sulphate of iron, in order to bring both processes into the same form. Thus  $\text{Fe} + \text{H}, \text{SO}_4 = \text{H} + \text{Fe}, \text{SO}_4$ . Here the acid is viewed as composed of hydrogen, and the salt as composed of

iron, combined with the compound  $\text{SO}_4$ , which is supposed to be the true radical of these compounds, and, although itself a compound body, to play exactly the same part as chlorine in hydrochloric acid and chloride of zinc. This may be rendered still clearer, by giving to the compound radical  $\text{SO}_4$  a single symbol  $\text{Su}$ , when the two processes will be thus represented :



We may use iron with hydrochloric, and zinc with sulphuric acid, with precisely similar results. And whichever view we take of the constitution of sulphuric acid and sulphates, it is at all events certain that in the case of both acids, the metal employed takes the place of the hydrogen, while the hydrogen is set free.

(The above simple apparatus for obtaining hydrogen gas is equally applicable in all cases where a gas is to be produced by the action of an acid on a solid body, without the aid of heat; as in the cases of dentoxide of nitrogen, sulphuretted hydrogen, carbonic acid, &c. It has, therefore, been described minutely, and will hereafter be referred to in describing the preparation of the above gases.)

*Properties.*—Hydrogen is a gas, colourless, tasteless, and, when quite pure, devoid of smell. When prepared from common zinc or iron, it contains some foreign body, which gives it an unpleasant smell. It is the lightest body known, its Sp. G. being 0.0694 (Air = 1), or 16 times less than that of oxygen, so that 100 cubic inches of it weigh only 2.14 grains. A lighted candle introduced into hydrogen, is extinguished, but the hydrogen takes fire at the mouth of the vessel, where it is in contact with the oxygen of the air, and burns rapidly away, giving out but little light, with an intense heat, and producing water, which, by proper means, may be condensed and collected. Hydrogen gas is not absorbed by water.

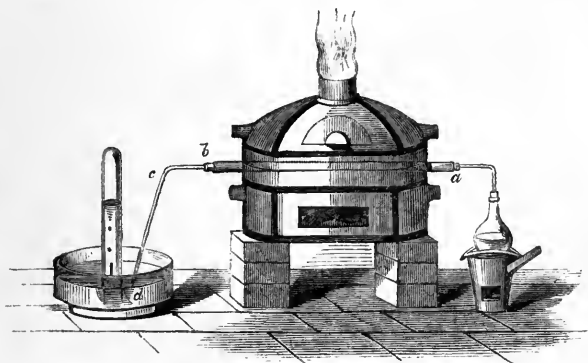
Hydrogen does not combine so readily with other bodies as oxygen does. It may be made, however, to combine with most of the metalloids and with a few of the metals. With chlorine, bromine, iodine, and fluorine, it forms powerful acids, the general formula of which is  $\text{HR}$  ;\* with carbon, sulphur, phosphorus, selenium, tellurium, and arsenic, it forms combustible gases, several of which have acid properties. With nitrogen it forms ammonia,  $\text{NH}_3$ , and probably two other compounds, ammonium,  $\text{NH}_4$ , and amidogen,  $\text{NH}_2$ .

\* R here stands for 1 eq. of any of the metalloids just mentioned.

From its extreme lightness, 100 cubic inches weighing only about 2·5 grs., while common air is about fourteen times heavier, hydrogen was formerly used for filling balloons. But owing to the abundance and cheapness of coal gas, the latter though much denser, is now universally employed for this purpose. On account of its greater density, it is necessary to use much larger balloons than when hydrogen was employed to fill them.

On the small scale, hydrogen is much used in chemical analysis, from its powerful attraction for oxygen, chlorine, bromine, iodine, fluorine, sulphur and selenium, at a red heat, to decompose compounds of metals with these elements. The oxide, chloride, sulphuret, &c., is placed in a horizontal tube, having one or more bulbs, and heated to redness, while a current of pure hydrogen is passed through the apparatus. The metal is usually left in a state of purity. This process is also applied in determining the composition of water as explained farther on, with a figure of the apparatus. (See p. 66).

Besides the processes above described, hydrogen is obtained by passing the vapour of water (steam) over red-hot iron wire,



when the iron is oxidised at the expense of the water, as in the figure; also by placing potassium or sodium in water, under a tube inverted, when these metals are instantly oxidised, and the tube filled with hydrogen; and by heating to redness a mixture of potash or soda, with organic matter, such as sugar, sawdust, &c.

#### HYDROGEN AND OXYGEN.

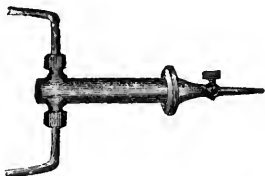
a. Water.  $\text{HO} = 9$ .

Hydrogen may readily be made to unite with oxygen, whether pure or in the form of atmospheric air. When hydrogen is

mixed with oxygen or with air, the mixture takes fire and explodes violently on the approach of a flame, or when the electric spark is passed through it. A jet of hydrogen, issuing from a tube, may be set fire to by the same means ; and in both cases, water is the only product.

We have already seen that 1 grain of hydrogen combines with 8 of oxygen to form water ; and as no other element takes up so large a proportion of oxygen, this is probably the reason why the combination of hydrogen with oxygen is attended with so intense a heat.

If hydrogen and oxygen be mixed in the exact proportion of 2 vols. of the former to 1 vol. of the latter, and the mixture set fire to, as it issues from a small tube, the most intense heat is produced that it is possible to obtain by combustion. The flame of the oxyhydrogen blowpipe, as it is called, readily melts platinum and pipe-clay, substances which resist the fire of the hottest furnaces. By this means, Mr. A. Kemp has melted 6 oz. of platinum at once.



The gases, if previously mixed, should be made to pass through a safety-apparatus before being set fire to ; but as accidents have occurred even when the safety apparatus was used, it is in all cases better

to keep the gases in separate gas-holders, and to allow them to mix only in the tube, just before they are ignited, regulating the flow of the two gases so as to obtain the most intense heat. Any excess of either gas cools the flame, and diminishes the effect. For the jet best adapted to this experiment, see the cut.

When a portion of spongy platinum, or of the finely-divided black powder of that metal, is introduced into a mixture of hydrogen with oxygen, or with air, the platinum soon becomes red-hot, and then the explosion instantly follows. Or if a jet of hydrogen be thrown on the metal in the air, it becomes red-hot and ignites the jet. On this principle is constructed the beautiful instantaneous light apparatus of Döbereiner.

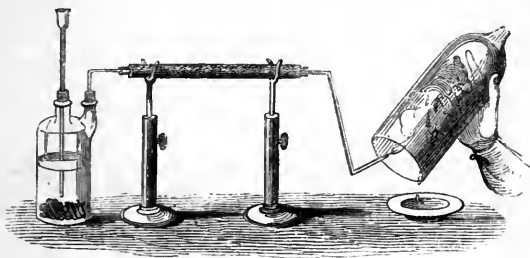
It would appear that the platinum possesses the property of causing hydrogen and oxygen to combine on its surface, whereby heat is developed sufficient to make the metal red-hot ; and it then acts as any other red-hot body, such as flame, would do, in causing the explosion.

The observations of Döbereiner on the properties of the black



powder of platinum may assist us to explain this singular property of platinum. He found that the powder condensed within its pores 253 times its volume of oxygen, and as the pores occupy only  $\frac{1}{4}$  of the bulk of the powder, this oxygen must be in a state of condensation such that it occupies only  $\frac{1}{1000}$  of its volume in the form of gas. In this state it must be denser than water, and we may easily conceive how it is thus rendered capable of at once combining with hydrogen. Spongy platinum only differs from the powder in being less minutely divided.

If a jet of hydrogen be set fire to and a cold dry bell-jar held over the flame, the inside of the jar will instantly be covered with a film of dew, which rapidly increases, and at last condenses into drops of water. See figure. This water, if collected, is found to be quite pure; and if a known weight of



hydrogen be burned, and the whole water collected without loss, the weight of the water will be 9 times that of the hydrogen; the difference, or 8 parts in 9 of water, is oxygen.

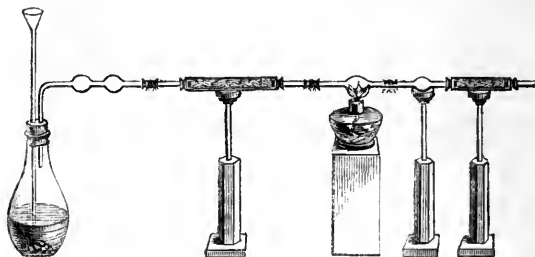
If the jet of hydrogen be set fire to, and a tube open at both ends held over it, so that the jet is some little way within the tube, a musical tone is produced. This depends on the combination of hydrogen with oxygen in successive small portions, each of which causes a slight explosion. These explosions following at short and equal intervals, throw the tube into vibration, producing a sound, the pitch of which depends on the width and length of the tube. The tube soon becomes moist from the formation of water.

This most important point, namely, the true composition of water, may be ascertained in other ways. Thus, if two vols. of pure hydrogen and one vol. of pure oxygen be mixed and confined over water or mercury, and if the electric spark be passed through the mixture, both gases will entirely disappear, and water alone will be the product. If the experiment be made in a graduated tube, and if, for example, 210 vols. of hydrogen be mixed with 100 vols. of oxygen, and the mixture exploded,

10 vols. of hydrogen will remain unchanged ; or if the proportions had been 200 vols. of hydrogen to 110 of oxygen, 10 of oxygen would have been left. Now, as hydrogen is 16 times lighter than an equal bulk of oxygen, it follows that 2 vols. of hydrogen must be 8 times lighter than 1 vol. of oxygen ; and thus we arrive at the same result as to weights as we obtain by burning hydrogen and weighing the water produced.

Another, and a very beautiful method, of ascertaining the composition of water, by weight, is the following :—

Into the bulb blown in the middle of a wide tube of Bohemian glass, the weight of which is known, there is introduced a weighed portion of oxide of copper. One end of the tube is then connected with an apparatus, from which a steady current of dry hydrogen is disengaged ; and to the other end is attached a tube containing fragments of chloride of calcium, a substance possessing a strong attraction for water ; this tube



with its contents being also weighed. As soon as the whole of the atmospheric air of the apparatus has been entirely displaced by the hydrogen gas, heat is applied, by means of a spirit-lamp, to the oxide of copper. Aided by the high temperature, the hydrogen very soon begins to decompose the oxide of copper, combining with its oxygen to form water ; and before long the black colour of the oxide is changed to the red of metallic copper. The water which is formed condenses in the cold part of the tube beyond the bulb, but by heating that part of the tube the whole of the water is soon carried by the current of gas into the tube with chloride of calcium, where it is retained. The apparatus is now allowed to cool, and when the tubes have again become full of atmospheric air, they are weighed. That with the copper will be found lighter than before, the other heavier. The loss of the former is oxygen, the increase of the latter is the water which that oxygen has yielded, and, of

course, the difference between the two is the hydrogen of the water.

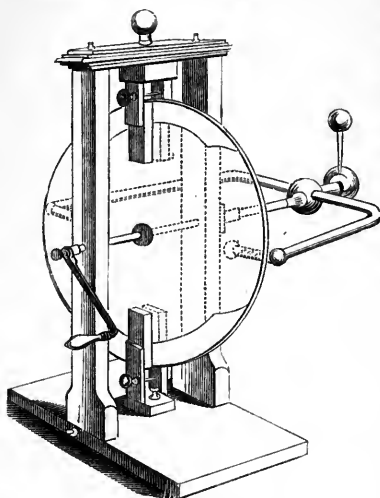
Let us suppose the first tube, when empty, to have weighed 500 grs., and when filled with the oxide of copper 540 grs., the oxide of copper must weigh 40 grs. The tube with chloride of calcium weighs, before the experiment, say 300 grs. Now, we should find, after the experiment, that the first tube now containing metallic copper, would weigh 532 grs. and the other tube 309 grs., the former having lost 8 grs. (oxygen), while the latter has gained 9 grs. (water). Hence, the 9 grs. of water contain 8 of oxygen, and, of course, 1 grain of hydrogen. Moreover, this experiment tells us that 40 grs. of oxide of copper are composed of 32 of copper and 8 of oxygen; thus proving the composition of water by synthesis, and that of oxide of copper by analysis.

There is still another method of demonstrating the composition of water: namely, the decomposition of that fluid by galvanic electricity. It is proper to say a few words as to the mode of obtaining a current of electricity, and the effects produced by that current on chemical compounds. The full consideration of the subject belongs to physics, and would alone require a volume; but we shall here mention such points as have the most direct and important bearing on chemistry.

Electricity, in the original and ordinary acceptation, is a term applied to the cause of a series of remarkable phenomena produced when certain substances are rubbed together. Thus, when glass or wax are rubbed with fur or silk, they acquire the power of attracting light bodies, which, however, are soon again repelled. It has been observed, that the peculiar state of the glass or wax may be communicated to other bodies, and may pass through metals, but is arrested by non-metallic bodies; and it is precisely those bodies which do not allow it to pass, or, to use the term applied to heat, which do not conduct it, that produce it when rubbed, so that it becomes sensible. Metals indeed also produce it by friction, but it is so rapidly conducted away to the hand, and thence to the earth (for the animal body conducts it), that it cannot be recognised, unless the metal have a handle of glass. Now such is the principle of the electric machine, in which a cylinder or a plate of glass is rubbed on a cushion of silk, and the electricity collected on a cylinder of metal supported on glass, or, as it is termed, insulated. The cushion must be in full communication with the earth by a wire or chain, otherwise the evolution of electricity soon ceases.

The reader will, no doubt, already perceive an analogy

between electricity and heat. Both are produced by friction (and, as we shall see, by chemical action); both are conducted by some bodies and not by others; both are imponderable.

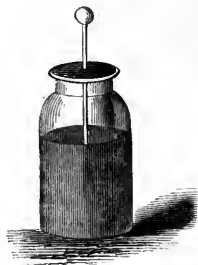


But this analogy extends much further; for just as we have heat and cold opposed to each other, so we have two forms of electricity, *plus* and *minus*, corresponding to heat and cold, and called positive and negative electricity. The electricity of rubbed glass is positive, that of wax or resin is negative. Moreover, just as heat gives rise to light or is converted into it, as when a body becomes red or white hot, electricity also gives rise to light; for whenever it passes suddenly from

one conductor to another through air, which is a non-conductor a bright spark of light is seen, and a snap or report heard. Again, heat produces electricity, and electricity produces heat for the electric spark is intensely hot; and we shall see that by galvanic electricity the very highest temperature may be produced. When we consider all these things, it becomes evident that whatever be the nature of heat, that of electricity is analogous to it; and as we speak of a current of heat passing along a conductor from a body charged with heat, or strictly with  $+$  heat, that is a hot body, to another which is cold, or relatively charged with  $-$  heat, so we speak of a current of electricity passing from a body charged with  $+$  electricity (or positive electricity) to one which is relatively charged with  $-$  electricity (negative electricity). One curious fact may be noticed here, that if a body be charged with either electricity or to use another and more exact form of expression, if electricity be either added to it (in which case it is positively charged, or charged with  $+E$ ) or taken from it (when it becomes negatively charged, or charged with  $-E$ ), any other body brought near it, instantly assumes the opposite state. This is called the induction of electricity.

It is further observed, that when two bodies thus *oppositely* electrified are brought near each other, they attract each other; but that if two bodies *similarly* electrified be brought near to each other, repulsion ensues. Hence a law which pervades these phenomena; namely, like electricities repel, unlike attract each other. Positive attracts negative, and negative attracts positive, but positive repels positive, and negative, negative. Thus when a light body, such as a pith ball, suspended by a silk thread, is brought near a body positively electrified, the ball becomes, by induction, negatively excited, and is therefore attracted; but as soon as it is in contact with the positive body, it forms part of it, becomes positively excited, and is then repelled. This explains why light bodies move backwards and forwards in such circumstances.

When an insulated metallic conductor, that is, one supported on glass, is strongly charged, and another conductor such as a metallic knob or the finger, approached, a spark passes, with a shock. This is the principle of the Leyden jar, which is a glass bottle or jar, lined with metal, and also coated with metal. When the brass ball is placed in contact with the machine, the internal metallic mass, from which proceeds a brass rod, ending in the ball, is soon highly charged, and when we form a communication between the outside of the jar, which should be in communication with the earth by a wire or chain, and the knob from the inside, the whole charge passes, with a loud report and bright flash, from one to the other.



The shock of such a jar, passed through the arm or body, is very severe, and a battery of 6, 12, or more large jars, of which all the insides are in metallic communication, and also the outsides separately, will give a shock capable of killing a small animal, or even one of considerable size. In fact, such a shock is a miniature thunderbolt, and by sending up a kite into a thunder-cloud, armed with a wire in the string, Franklin obtained from the end of the wire, sparks identical with those of the battery. The experiment is dangerous, for a Russian philosopher who repeated it, happening to stand too near the wire at the moment that it became very highly charged, was killed on the spot. His servant saw a ball of light pass from the wire to his master's head.

The above brief remarks will show how the lightning has been identified with electricity, and why we speak of the electric fluid and electric currents, although, in truth, we do not know

that there is such a fluid at all. We only observe certain states, the causes of which are quite unknown ; but as these resemble the phenomena which would be produced by the passage or the accumulation of a subtle imponderable fluid, we use that language ; this, however, it must be remembered, is entirely hypothetical.

The electricity above briefly noticed is called common, or friction electricity. Its chemical influence is marked, but limited, from the peculiar form it takes, and the violent action of large quantities. A very small electric spark, however, accompanied by a hardly audible snap, will cause many gases to combine, often with explosion. This is the case with oxygen and hydrogen, with hydrogen and chlorine, &c. A succession of sparks, passed through a portion of air, causes the formation of a little nitric acid from the nitrogen and oxygen. And in the same way some gases may be decomposed.

But there is another form of electricity, namely galvanic electricity, which is far more important to the chemist, both from its origin, which is chemical action, and its valuable applications in chemistry. Be it observed, however, that it is essentially the same as the other ; that it appears as positive, and negative, or  $+E$  and  $-E$ , that it is conducted by the same bodies, and finally, that its chief peculiarity is, that it has a low intensity while its quantity is large, while common electricity appears in small quantities, but with extreme intensity. The difference may be illustrated by comparing a cubic yard of any matter at blood heat, which of course contains an immense *quantity* of heat of low *intensity*, with a cubic inch of matter at a white heat, where the *quantity* of heat must be far less, inasmuch as it would have no sensible effect in raising the temperature of the tepid mass, but where the *intensity* is very exalted. Faraday has calculated that the quantity of electricity required for the decomposition of one grain of water far exceeds that contained in a thunderbolt, while its intensity is so low, that it is not perceived as a shock when passed through the hand.

Whenever two bodies act chemically on one another, electricity is developed, just as heat is, and by proper arrangements, this electricity may be conducted as we please. It is impossible here to enter into details as to the innumerable forms of apparatus, or galvanic batteries, as they are called, which have been employed for various purposes. The general principle of all of them is to form what is called a galvanic circuit, or pair of elements, and to combine together as many such pairs as may be required.

A galvanic circuit may be formed of one metal with two

liquids, but it is better to employ two metals, or one metal and charcoal (in that form in which it conducts electricity) with one liquid, which is generally an acid. The combinations most used are, zinc, copper, and diluted sulphuric acid ; zinc, platinum and nitric acid ; zinc, charcoal, and nitric acid ; and zinc, platinised silver, and diluted sulphuric acid.

When a piece of zinc is immersed in dilute sulphuric acid, so weak as hardly to act on it, and when a piece of copper is also immersed in the liquid, no change occurs, so long as the metals are not in contact or in communication. But if they be made to touch in the liquid, or if a copper wire from the one metal be made to touch a similar wire from the other, out of the liquid, a brisk action at once begins, and the zinc is rapidly dissolved, the copper remaining unacted on.

Now this simple arrangement is a galvanic circuit. For if we examine the wire while contact is preserved, we find that a current of electricity is constantly passing along it. This is easily shown by placing a magnetic needle under the wire, when the needle will place itself at right angles to the wire, which, in fact, is magnetic as long as the current passes. Or if the plates of metal be of some size, and the current be made to traverse a fine platinum wire in passing from one wire to the other, for about a quarter of an inch or less, the platinum wire will become hot, perhaps red-hot.

Again, if one of the wires be made to end in a small disc of metal, on which is laid a piece of paper moistened with a solution of starch containing a little iodide of potassium, and if now a similar disc attached to the other wire, be laid on the paper, the current will pass, and in doing so, will decompose the iodide, and the starch will be coloured blue by the liberated iodine.

These facts prove that a current of electricity passes along the wire from one metal to the other, to use the language commonly employed, and show at all events that a change takes place in the wire, and that an influence of some kind traverses it, whatever be the nature of that influence, whether it be conceived to be, like light, a peculiar form of motion in the particles of a supposed ether, or regarded as a fluid.

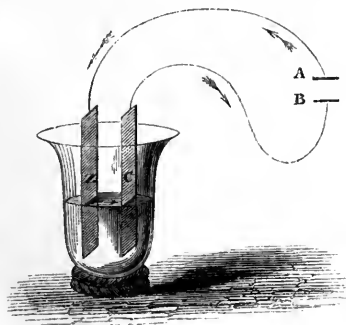
It is found that when two metals, such as zinc and copper, are placed in contact, especially if moist, electricity is developed, and the zinc is found to be positive, the copper negative. Hence we say that the current passes from the positive or  $+$  side, the zinc, to the negative or  $-$  side, the copper, or platinised silver. This takes place *in* the conducting liquid, but of course, *out* of the liquid, the current passes from the copper plate along the wire, back to the zinc, when the wires are in contact. See the

figure, where *z* represents the zinc plate, and *c* the copper plate. The arrows show the direction of the current, *A* and *B* are two small discs of platinum, which here represent the opposite poles, or electrodes, as they are called, because they give passage to the electric current.

Now this current is one of low intensity and of large quantity. It passes readily through metals, and through many liquids, such as acids and saline solutions. But in doing so it decomposes either the liquid or some of the dissolved matters, as, for example, the iodide of potassium in the experiment above described. And when a compound is thus decomposed, its elements, in virtue of the law of electrical attraction, go to the opposite sides of the circuit, the opposite poles or electrodes, as they are called. In the above case, for example, the potassium, being strongly positive, goes to the negative electrode, that is, the wire from the zinc plate (where it does not appear, being oxidised by the water), while the iodine being negative appears at the positive electrode, that is, the wire from the copper plate. It will be found that the blue colour appears only on the side of the paper next the copper plate.

If the current be too weak to pass through the liquid, (and it must do so to get from the zinc plate to the copper, and also to pass through the moist paper,) no decomposition takes place. But this may be remedied either by diminishing the distance between the plates, or by adding some other pairs to increase the intensity of the current.

A feeble current suffices to decompose iodide of potassium, but it requires a very powerful one to decompose some com-



pounds, such as potash and soda. Water may be decomposed, and that pretty rapidly, by the current from six pairs of Smee's plates, which are made of platinised silver, with zinc on both sides, and are five inches long by four broad. This combination, charged with sulphuric acid diluted with six or eight parts of

water, gives a powerful steady, and long continued current. In fact, it continues until the acid is saturated or the zinc exhausted, when, of course, one or other must be renewed.



We do not know how it happens that the electric current decomposes chemical compounds. It may be that the elements becoming strongly and *similarly* electrified, repel each other, and are attracted, each by the electrode having the opposite electricity to that which the elements naturally possess. But then if the elements be similarly electrified when they separate, they should be attracted by the same electrode; and again, if they become, after separation, oppositely electrified, so as to be attracted to different electrodes, they ought again to combine. It has been supposed that at the electrode where the positive electricity enters the liquid to be acted on, it attracts from the first molecule of the compound (say iodide of potassium), the negative element iodine, setting free the potassium of that molecule, which seizes the iodine of the next, and so on through the chain of molecules to the other electrode, where the potassium of the last is separated and attracted by the electrode. But it is not easy to see how the iodine in the second molecule should quit one atom of potassium to unite with another, unless the latter be supposed to have, for the moment, superior positive energy, which it must transmit to the other. All this, however, is obscure, and all that is certain is, that the two elements appear at opposite electrodes.

On this fact is founded the electrical arrangement of the elementary bodies. Oxygen, in whatever compound it occurs, always appears, when separated, at the positive electrode; potassium and hydrogen nearly always at the negative electrode. Hence we conclude that oxygen is negative compared with all other elements, and hydrogen and potassium positive. Chlorine, when separated from its compounds with hydrogen or metals, always appears at the positive electrode, and is, therefore, negative with respect to them; but when its compounds with oxygen are decomposed, it appears at the negative electrode, and is, therefore, positive with respect to oxygen. The same is true of bromine, iodine, sulphur, &c.; and of the metals, while potassium and sodium are the most highly positive, gold and platinum are the most negative, although still strongly positive with respect to oxygen, chlorine, sulphur, &c. The other metals stand between these extremes.

The current of a powerful battery will decompose such bodies as potash or soda, the metals of which appear at the negative electrode, and there burn and are oxidised, if not at once placed in naphtha. These metals were thus discovered by Davy. A similar current, if made to pass through thin leaves of metal, causes them to burn with great splendour; and if two poles be armed with points of dense and well conducting charcoal, and

these points brought within a small distance of each other, the passage of the current from one to the other produces an arch of dazzling white light, the most brilliant artificial light which it is possible to produce. This is called the electric light; and the chief difficulty in its use is, that the charcoal points rapidly wear and lose their shape, thus deranging the distance. The best battery for producing the electric light is Bunsen's, formed of compact charcoal, zinc, nitric acid, and diluted sulphuric acid. This battery gives for a long time a powerful and nearly uniform and constant current, and it may be so used that either the elements act separately, or are combined so as to act like one pair of very large surface. It has also the advantage of superior cheapness over those forms of battery in which platinum is employed, such as Grove's and Smee's. In fact, charcoal, in the state in which it is used for this battery, is even more negative than platinum. With six of Bunsen's elements a very good electric light may be obtained; but with twenty or thirty, it is dazzling in the extreme.

Another most interesting and valuable application of the galvanic current is that called the electrotype. This may very easily be practised with one pair of Smee's plates. To the wire from the zinc plate is attached the model to be copied, the surface of which (if it be of wax, fatty matter, or plaster of Paris), is covered with powdered plumbago, to render it capable of conducting electricity, and it is then suspended in a saturated solution of blue vitriol, or sulphate of copper, to which a little free acid has been added. From the other wire is suspended, opposite the model, and within a short distance, a stout plate of copper. The current passes through the solution, and decomposes the oxide of copper, the copper of which is deposited on the model at the negative pole, but in a state as solid and coherent as if melted and forged, and takes a perfect copy, reversed of course, of the model; while the oxygen is carried to the positive pole, and there combines with and dissolves the copper of the suspended plate, so that the liquid is kept constantly saturated—a point of great importance for the regular march of the process. In about 24 hours, or longer if the weather be cold, the deposit of copper is thick enough for all purposes, and it is found that the weight of the deposited copper is precisely equal to the loss of weight in the copper-plate at the other pole. The acid in the vessel where the galvanic pair is immersed, must not be too strong, for a slow decomposition is far preferable to a rapid one. When silver or gold is to be deposited, solutions, usually, of certain double cyanides of these metals are substituted for the salt of copper,

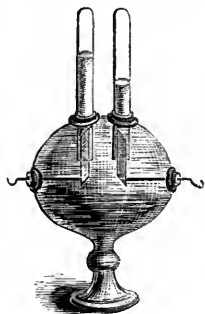
and a plate of silver or gold for the copper one. Of course, if we wish a true copy of the object, we take the first electrotype, which is reversed, and gently greasing its surface, taking care to wipe off all superfluous grease, we use it as the electrode, or nucleus, for deposition. Or we begin by making a hollow cast or mould in plaster, stearine, or fusible metal, of the object, and the copper deposited on this is a true, and not a reversed, copy of the original.

In this way an engraved copper-plate may be copied, and a sufficient thickness of copper deposited to yield a stout plate, which is found even tougher and harder than forged copper, and on whose surfaces the minutest traces of the graver, and even all the imperfections of the engraved plate, are faithfully reproduced.

There are numerous forms of electrotyping apparatus ; but we have here described one of the simplest and best, which any one who has a Smee's pair of plates can set up, and which yields excellent results.

Let us now return to the application of galvanic electricity to the analysis of water.

When the electric current of a powerful battery is made to pass through water in an apparatus so contrived, that the gas given off at each electrode may be received into a separate graduated tube, it is found that by the time the tube at the positive electrode is half full, the tube at the negative electrode is quite full ; and on examination, the gas in the latter is found to be pure hydrogen, while that in the former is pure oxygen ; and the proportion, by volume, is obviously 2 of hydrogen to 1 of oxygen, and from this, by means of the specific gravities of the gases, we obtain, as before, the proportion, by weight, of 1 to 8.



Water, which is thus proved to contain 1 eq. of hydrogen to 1 eq. of oxygen, represented by  $\text{HO}$ , is, at ordinary temperatures, a liquid, colourless, tasteless, and inodorous. It assumes the solid form, that of *ice* or *snow*, at  $32^{\circ}\text{F}$ ., and all lower temperatures, and often crystallises beautifully. A few of the forms of snow are here given. It takes the form of gas or vapour, that of *steam*, at  $212^{\circ}\text{F}$ ., and retains that form at all higher temperatures.

When ice is heated above  $32^{\circ}$  it melts into water ; and when steam is cooled below  $212^{\circ}$ , it condenses into water. Thus

water possesses the liquid form only at temperatures lying between  $32^{\circ}$  and  $212^{\circ}$ .

We may here introduce a few remarks on the effects of heat upon matter. When heat is applied to a body in the solid



form, the first effect is to increase its bulk or to expand it; and this goes on, the expansion increasing with the heat. Hence, all solids are more bulky when hot than

when cold, and when a solid is cooled, it always shrinks in volume, but expands again on being heated. The only apparent exception to this law is when heat decomposes a substance, or alters its composition. Thus clay, dried in the air, shrinks when heated to redness, because water is expelled. The perfectly dry clay obeys the usual law.

The thermometer is founded on the expansibility of matter by heat; but as solids are rarely used, we shall return to this subject under the expansion of liquids.

But when solids are heated to a certain point, another change ensues: they become liquid or melt. Thus, ice at  $0^{\circ}$  will expand if warmed, till it reaches  $32^{\circ}$ , but then it melts. Each body has its own melting point. Mercury melts at about  $40^{\circ}$ , or  $72^{\circ}$  below the melting point of ice, and is solid at all lower temperatures. Sulphur melts at about  $240^{\circ}$ , and tin at  $442^{\circ}$ , while many metals require a red or even a white heat to melt them.

Liquefaction is attended with the disappearance of a large amount of heat, which becomes insensible to the hand or to the thermometer, and goes to produce the liquid state. This fact is easily proved; for if ice be placed in a pan over a hot fire, it will melt slowly, and will not become warmer by one degree so long as any ice remains unmelted, although heat is pouring into it in large quantities. Or if we take a pound of liquid water at  $32^{\circ}$ , and a pound of ice at  $32^{\circ}$ , and add to each 4 ounces of water in the shape of steam (which, as we shall see hereafter, gives out much heat), the pound of ice will be simply melted, but not at all warmed, while the pound of water will be warmed to a considerable extent. Here the heat applied to the ice has only served to liquefy it, and has become insensible, or as it is termed, latent.

For the same reason, when a solid is suddenly liquefied at the ordinary temperature, cold is produced, because the melting body takes from the surrounding ones the heat required to melt it. This is the principle of freezing or frigorific mixtures, in which snow is usually suddenly melted by mixture with certain salts, which are also liquefied or dissolved.

Conversely, when a liquid is suddenly rendered solid, the heat which had liquefied it, and had become latent, becomes again sensible, and the temperature rises. Water may be cooled, under certain circumstances, far below  $32^{\circ}$  without solidifying: but if agitated, it instantly becomes ice, and the temperature rises to  $32^{\circ}$ , in consequence of the latent heat being set free. Hence, also, when a mass of water is exposed to intense cold, say to a cold  $0^{\circ}$ , or of  $40^{\circ}$  below  $0^{\circ}$ , the temperature of the water never falls below  $32^{\circ}$  till the last drop is frozen, because each drop that freezes gives out its latent heat, or heat of fluidity, and the temperature cannot fall as long as any liquid water remains. This renders the freezing of large masses of water a very slow operation, fortunately for us. There is, however, another cause for this, to be afterwards mentioned.

What is true of the melting and solidification of ice or water, is true of all such bodies as are not decomposed by heat, the melting or solidifying point varying for each substance.

Water, or ice, once liquid again obeys the law of expansion by heat, with a very curious exception, for it only does so from  $39^{\circ}$  or  $40^{\circ}$  upwards to  $212^{\circ}$ . Between  $32^{\circ}$  and  $39^{\circ}$  water actually contracts a little as it is warmed, or expands in cooling from  $39^{\circ}$  to  $32^{\circ}$ ; its greatest density being at  $39^{\circ}$  or  $40^{\circ}$ . Hence, water at  $39^{\circ}$ , when cooled, becoming lighter, remains at the surface till frozen, when it becomes still lighter. For this reason, the freezing of water proceeds very slowly from the surface downwards, ice being a very bad conductor of heat; and at no great depth, the water may be at  $39^{\circ}$ , unless the frost lasts for weeks or months. This cause of slowness in congelation is added to that of the latent heat developed. Were it not for the combined operation of these two causes, every pond and lake would be frozen solid every winter, and as melting is as slow as freezing, the summer might not suffice on all occasions to melt the whole. It is well known that very deep lakes are never frozen, even at the surface, in our climate, because it takes so long to cool down the mass of water. The first portion cooled below  $39^{\circ}$  rises to the surface, and being further cooled, remains there, and is, to a certain extent, protected from the cold of the air by the contact of the warmer and heavier water below. But even in the severest

frost, only a thin crust of ice can be formed on the surface of deep water. This curious anomaly in regard to the action of heat on water between  $32^{\circ}$  and  $39^{\circ}$  seems to occur only in water.

Above  $39^{\circ}$  water, like other liquids, expands when heated, and it might be used for thermometers, but for its liability to freeze and burst the tubes; for ice, being lighter, is more bulky than water, and freezing water will rend the toughest metals, or even rocks. Besides this, water boils too easily to be convenient for thermometers. Consequently for measuring cold, alcohol, or spirit of wine, which cannot be frozen, is employed, and for higher temperatures, mercury which boils at about  $600^{\circ}$ , is taken. The mercurial thermometer is first placed in melting ice, and the height of the liquid marked. It is then transferred to boiling water, under the pressure of 30 inches of the barometer, and its height again marked. The space between the two marks is divided, in this country, into 180 degrees, and the graduation continued 32 degrees below the freezing point, or to  $0^{\circ}$ . The zero of Fahrenheit was first obtained by using a mixture of snow and salt; but that was found variable, although his division and his zero have been retained. In the centigrade scale, used on the continent, the zero is placed at the freezing point, and the space between that and the boiling point divided into 100 degrees. Hence,  $5^{\circ}$  centigrade are equal to  $9^{\circ}$  Fahrenheit.  $32^{\circ}$  on Fahrenheit's scale corresponds to  $0^{\circ}$  on the other, and  $212^{\circ}$  to  $100^{\circ}$ . Thermometers are now made with the two scales marked on opposite sides of the stem.

If we wish to reduce degrees of the centigrade scale to those of Fahrenheit, we must multiply by 9, divide by 5, and add  $32^{\circ}$ ; because the zero of the latter is  $32^{\circ}$  lower. To reduce Fahrenheit's degrees to centigrade ones, subtract  $32^{\circ}$ , multiply by 5, and divide by 9. The student who, from reading continental works, has occasion often to perform this operation, will do well to construct for himself a table of the two scales, or to procure one of the thermometers with double scale above alluded to.

Water, then, when heated, expands regularly till it reaches  $212^{\circ}$ , when a sudden change occurs, and it is converted into a gas, or vapour, which is called steam. Every other liquid undergoes a similar change, but each at its own point, which is called the boiling point. Alcohol boils at  $176^{\circ}$ , ether at  $96^{\circ}$ ; sulphuric acid and mercury at about  $600^{\circ}$ , and so on. Several things are to be observed about this change, which we shall follow in the case of water.

In the first place, the liquid, when converted into gas, is prodigiously increased in volume. The gas, vapour, or steam of water, occupies 1400 times the space of the water from which it

is derived. That of ether is only 500 or 600 times the volume of the liquid. This may easily be shown by placing a little ether on the top of a quantity of water in a long tube, closed below, so that the last inch at the open end is filled with ether; then, closing the tube with the finger, and inverting it, with the open end under water in a basin or trough. The ether now rises to the closed end, and if the water be coloured, is easily seen at some distance. Hot water is next poured over the upper and closed end of the tube; this converts the ether into vapour,—that is, causes it to boil, and by the time a fourth or fifth part of it has been vaporised, the vapour has nearly filled the tube, and forced down the water to the level of the trough. By pouring cold water on the tube, the ether is again liquefied, and the water rises to its original level; and these changes may be repeated as often as we please, forming a striking and beautiful class experiment.

It is on this principle that the steam raises the piston in the steam-engine, and when the steam is again condensed or liquefied by a jet of cold water, the piston falls, and the alternate motion thus obtained is converted into a rotatory one by machinery.

Another circumstance is this. Every substance, when in the form of gas, is perfectly *elastic*,—that is, its volume varies, the temperature remaining unchanged, inversely as the pressure to which it is subjected. The bulk of solids and liquids is not perceptibly affected by pressure. If a gas under one atmosphere occupies 100 volumes, under two atmospheres it will occupy 50 volumes, under five atmospheres 20 volumes, and so on; and under  $\frac{1}{2}$  an atmosphere, it will expand to 200 volumes, &c. &c. All gases are equally elastic, so long as no part of them is liquefied,—that is, above their boiling points.

The next point to be noticed is, that the boiling point depends, not on the temperature alone, but on the temperature combined with the atmospheric pressure. Since 100 cubic inches of air at the earth's surface and at the level of the sea weigh about 31 grains, it is plain that the atmosphere, though relatively light, must have an immense absolute weight. It consequently presses on the earth, as will be more fully shown in treating of air, with a force which has been found to amount to nearly 15lbs. on every square inch. Now this pressure directly opposes the conversion of water into steam or gas, and this is the reason why water must be heated to  $212^{\circ}$  before it boils. At that point the repulsion caused by heat overpowers both the force of cohesion and the pressure of the air. When the pressure is diminished, water boils at a lower temperature. This may be shown by

taking boiling water from a kettle, placing it under the bell-jar of the air-pump, and exhausting the jar of its air. The water, which has long since ceased to boil, and is a good many degrees colder than  $212^{\circ}$ , soon begins to boil briskly. In a vacuum water may be made to boil by the heat of the hand. For a similar reason, water boils at a lower temperature on the top of a mountain than at its foot, being pressed upon by a less column of air in the former case. For every 430 feet we ascend, the boiling point falls 1 degree; and the height of mountains may be accurately measured by comparing the boiling point of water at the summit and at the sea-level at the same time. Again, the natural variations of the atmospheric pressure affect the boiling point of water, although, of course, only to a small extent. It is only under an atmospheric pressure equal to 30 inches of mercury that water boils exactly at  $212^{\circ}$ .

If the pressure be artificially increased, as in a closed vessel, such as a digester, or in a high pressure engine boiler, the boiling point rises; and when it has thus been raised considerably, if the pressure be suddenly reduced to the ordinary amount by opening the stopcock or valve, the temperature rapidly falls to  $212^{\circ}$ , while a prodigious amount of steam is given off.

Thirdly, when water is converted into gas or steam, a large amount of heat disappears, just as in the melting of ice. Place cold water over a hot fire. It rapidly becomes warmer, till at last it reaches  $212^{\circ}$  and boils. From that moment, even if the fire be increased tenfold, the temperature never rises a single degree till the last drop of water is vaporised. The vast amount of heat which enters it becomes latent in the steam, or is consumed in giving the gaseous form, but does not affect the temperature. As the quantity of heat that thus disappears in forming steam is very great, much greater than is required to vaporise many other liquids, the boiling of water is not only tedious, but consumes a great deal of fuel.

When steam is again condensed or liquefied, all this latent



heat reappears, and becomes sensible. Hence steam is very useful for heating liquids or air, but can never give a heat beyond  $212^{\circ}$ , since at and above that point the steam is not liquefied. Hence, also, a scald from steam is far more severe than one

from boiling water. The latter only gives out the difference of



sensible heat; the former yields, in addition, all its latent heat. It is for this reason that 4 oz. of *steam* at  $212^{\circ}$  will bring 1 lb. of water at  $60^{\circ}$  to the boiling point, without losing its own temperature of  $212^{\circ}$ , while 4 oz. of *water* at  $212^{\circ}$ , added to 1 lb. of water at  $60^{\circ}$ , only render it lukewarm, and the hot water itself becomes also lukewarm. The figure shows the use of steam for evaporating liquids. Such an arrangement is called a water-bath.

Although water only *boils* at  $212^{\circ}$  (under the usual pressure), yet it is slowly vaporised at all temperatures. This is called evaporation as distinguished from boiling or ebullition, both being modes of vaporisation.

Water at  $32^{\circ}$ , nay, ice at  $32^{\circ}$ , and at still lower temperatures, evaporates, and gradually disappears. Thus, in long-continued dry frost, after a fall of snow, the snow rapidly evaporates, and disappears where it is thin, without melting. At all ordinary temperatures, water constantly evaporates, but silently, and without any appearance of bubbles of gas, because the whole operation goes on at the surface only.

Evaporation is promoted by heat, by the dryness of the air, by wind, and by diminished pressure; it is impeded by cold, by increased pressure, by calm weather and by a moist atmosphere. It is a most important process; for by it all the water of the earth's surface rises into the atmosphere, whence it is returned as rain, dew, hail, or snow, to find its way to the sea, from which, as well as from the land, rivers, and lakes, it again rises, again to fall, and is thus kept continually circulating through the atmosphere, where its presence is equally essential to animal and to vegetable life.

In evaporating, as well as in boiling, for the change is the same in both cases, except in the time required, water absorbs or causes to disappear, and become latent, the same large amount of heat formerly explained. Consequently evaporation at the ordinary temperature produces cold, and the more intense, the more rapid the evaporation. Water may easily be frozen by its own evaporation in *vacuo*; that is, the evaporation of a part cools the remainder to  $32^{\circ}$ . Nay, in warm climates, water is actually frozen during the night, if placed in shallow vessels and in circumstances favourable to evaporation. In *vacuo* the evaporation is soon checked by the atmosphere of steam formed, which presses on the water. But if some substance be at hand which absorbs the steam, evaporation recommences, and in this way water may be frozen in *vacuo*. In Wollaston's cryophorus, the atmosphere of steam is condensed by the use of ice, applied to one ball of the apparatus, and by this cold so applied, the water

in the other ball, which may be several feet distant, is soon frozen by its own evaporation.

If we wish to evaporate a liquid at the ordinary temperature, and yet pretty rapidly, we place it under a bell-jar, as in the figure, and we may either exhaust the air of the jar, or leave it full of air. In either case we place along with the liquid to be evaporated, a flat vessel with oil of vitriol, or else with quick lime, to attract the aqueous vapour, and thus promote evaporation.



A mixture of liquefied carbonic acid and ether evaporates so rapidly at very low temperatures, as to yield a cold of more than  $100^{\circ}$  below zero, and in this way several pounds of mercury may be frozen in a minute or two. By the evaporation, in vacuo, of liquefied gases, such as carbonic acid, sulphurous acid, and nitrous oxide, Faraday has produced the most intense cold yet obtained, about  $200^{\circ}$  below zero.

Steam, at all temperatures above  $212^{\circ}$ , is a perfect gas, in all respects similar to common air, oxygen or hydrogen, in physical properties. Like them it expands when heated, and contracts when cooled. The only difference is that it can be liquefied if cooled below  $212^{\circ}$ , while air, oxygen, hydrogen, and nitrogen have never yet been liquefied, even by the intense cold just mentioned, aided by a pressure of many atmospheres. But it cannot be doubted that these gases would be liquefied if we could cool them sufficiently, and that they are the vapours of extremely volatile liquids, as steam is the vapour of water. About thirty years ago none of the so-called permanent gases, that is, bodies gaseous at ordinary temperatures, had been liquefied. But first, chlorine, then cyanogen gas, was liquefied by a pressure of from two to three atmospheres, and sulphurous acid gas was found to liquefy under the ordinary pressure if cooled down to  $10^{\circ}$ . Subsequently ammonia, sulphuretted hydrogen, and carbonic acid were liquefied, the first by seventeen atmospheres, the last by thirty-six to forty atmospheres, and carbonic acid was frozen to a solid mass like snow, by its own evaporation. More recently almost all the known gases, except the three elementary ones above named, oxygen, hydrogen, and nitrogen, have been liquefied, nitrous oxide requiring the immense pressure of fifty-six atmospheres to condense it. It is evident then that the uncondensed gases, such as oxygen, the condensable gases, such as nitrous oxide, car-

bonic acid and chlorine, and the vapours of bodies liquid at ordinary temperatures, such as the vapours of water, alcohol, and ether, are all equally gases, and all equally the vapours of bodies whose essential form is the solid form, and which, by combining with different proportions of heat, become first liquid and then gaseous. Iron and gold may be melted in a furnace, but cannot be boiled or rendered gaseous by any heat at our command; and on the other hand, oxygen, hydrogen, and nitrogen cannot as yet be liquefied by any cold in our power to produce. The boiling point of iron is perhaps  $5000^{\circ}$  above zero; that of oxygen may be  $1000^{\circ}$  below zero. The student will therefore bear in mind that vapours and gases are essentially the same, but that we generally use the term vapour when speaking of the gases of bodies which are solid or liquid at the ordinary temperature.

In a few cases, such as those of iodine, arsenic, and camphor, solid bodies, under the ordinary pressure, pass at once into the gaseous state without melting. This is because under that pressure, their boiling point is a little below their melting-point. But if the pressure be increased, as by heating them in hermetically sealed tubes, they may be melted like other bodies.

Such are, in a general way, the effects of heat on water in its various forms, and as has been intimated, it affects other bodies in the same way, each body having its own melting or congealing point, and its own boiling or condensing point. Let us now return to the consideration of water.

In certain arctic regions water is always or nearly always, solid. Even in that state, however, and at all temperatures below  $212^{\circ}$  it is always slowly assuming the gaseous form. It is in this way that watery vapour is constantly rising into the atmosphere from the surface of the sea, of lakes, of rivers, and of the soil; which watery vapour, being again condensed into the liquid form, falls back on the earth in the shape of rain or dew, or if frozen, as snow, hail, and hoar-frost.

Water is perfectly neutral; that is, it exhibits in itself neither acid nor basic properties; but is capable of combining with both acids and bases, and indeed seems to be almost essential to their activity. The compounds of water with acids and bases are called hydrates; as  $\text{HO}$ ,  $\text{SO}_3$ , hydrated sulphuric acid, and  $\text{KO}$ ,  $\text{HO}$ , hydrate of potash.

Water combines also with neutral salts, and that in two conditions. In one it is easily expelled by heat, and the salt, if crystallised, generally falls to powder when the water has been expelled. This is called water of crystallisation, and its quantity is often very large. In the other, a portion of water,

generally 1 eq., is combined with the salt by so powerful an affinity that it is with some difficulty separated. This is called saline water, because it may be replaced by an equivalent of a neutral salt. In formulæ, water of crystallisation is represented by aq. (for aqua), and saline water by HO. Thus, green vitriol is represented by  $\text{FeO}, \text{SO}_3 + \text{HO} + 6 \text{ aq.}$  : that is 1 eq. of neutral sulphate of protoxide of iron, 1 eq. of saline water, and 6 eq. of water of crystallisation. When this salt is gently heated, the 6 eq. of water of crystallisation are expelled, but the 1 eq. of saline water can only be expelled by a red heat. It can also be replaced by a neutral sulphate, such as sulphate of potash,  $\text{KO}, \text{SO}_3$ , and the resulting double salt is  $\text{FeO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{ aq.}$  Here as in the green vitriol, the 6 eq. of water of crystallisation are easily expelled by a gentle heat.

In relation to acids, therefore, water acts the part of a base ; in relation to bases, that of an acid ; and in relation to neutral salts, that of a neutral or indifferent substance, or indeed, of a neutral salt. Taking the three examples of hydrated sulphuric acid, HO,  $\text{SO}_3$ , hydrate of potash, KO, HO, and dry sulphate of iron,  $\text{FeO}, \text{SO}_3 + \text{HO}$ , it is to be observed that the water in the first can only be replaced by a base, such as potash, KO, which would yield sulphate of potash,  $\text{KO}, \text{SO}_3$  ; the water in the second can only be replaced by an acid, such as sulphuric acid,  $\text{SO}_3$ , which would yield the same salt,  $\text{KO}, \text{SO}_3$  ; and the water in the third may be replaced by a neutral salt, such as sulphate of potash,  $\text{KO}, \text{SO}_3$ , which would give rise to the double salt,  $\text{FeO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ . Water in these three different characters is called basic water, hydratic water, and saline water, and, in addition to these, we have water of crystallisation.

Many salts containing water of crystallisation, lose a part or the whole of it, when exposed to air, and these are said to be efflorescent, or to effloresce, because they become opaque and powdery on the surface. The sulphate, phosphate, and carbonate of soda are highly efflorescent. Other salts attract water from the air, and finally liquefy ; these are said to be deliquescent, or to deliquesce. Carbonate of potash, nitrate of lime and chloride of calcium are very deliquescent.

Besides the numerous forms of combination, in which water most frequently loses the liquid form, it enters, as a liquid, into a peculiar kind of combination with the greater number of all known substances : it dissolves them. Of all liquids, water is the most powerful and general solvent, and on this important property its use depends. By the solvent power of water, substances, inert in the solid form, are made to assume the liquid

form, and thus to become active—chemical action is promoted—substances mixed together may be separated from one another;—in short, without water, not only the operations of the chemist, but the processes of animal and vegetable life, would come to a stand.

The solvent power of water, in regard to solid bodies, is generally increased by heat. Hot water, therefore, dissolves more of most bodies than cold water does; so that when a hot saturated solution cools, it deposits a quantity of the dissolved solid, commonly in crystals.

Water readily dissolves or combines with, or absorbs, as it is termed, many gaseous bodies. The gas, in this case, assumes the liquid form; and as heat tends to cause bodies to assume the gaseous form, it is obvious that heat must diminish, and cold increase, the solvent power of water for gases. Increased pressure also enables the water to absorb more of a gas than it will do under the ordinary pressure, evidently because pressure favours the liquefaction of a gas, by forcing the particles nearer to each other.

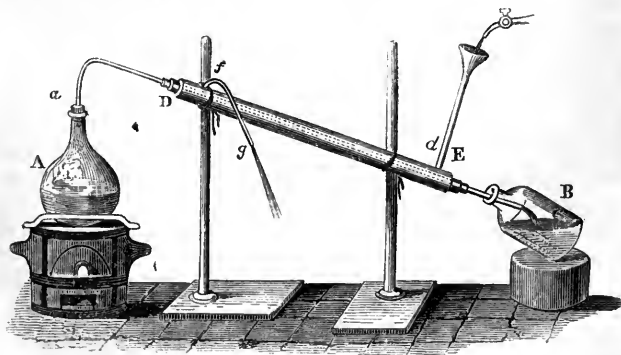
In consequence of the great solvent power of water, it is never found pure in nature. Even in rain water, which is the purest, there are always traces of carbonic acid, ammonia, and sea-salt. When the rain water has filtered through rocks and soils, and re-appears as spring or river water, it is always more or less charged with salts derived from the earth, such as sea-salt, gypsum, and chalk, the latter dissolved as bicarbonate of lime by an excess of carbonic acid. When the proportion of these is small, the water is called soft; when larger, it is called hard water. The former dissolves soap better, and is therefore preferred for washing; the latter is often pleasanter to drink, as its saline contents and its free carbonic acid communicate to it a slight, but agreeable taste.

When water becomes so highly charged with foreign matters as to have an unpleasant taste, or to acquire medicinal virtues, it is called mineral water. Of mineral waters there are several kinds: those in which iron predominates are called chalybeate waters; where sulphur prevails, they are called sulphureous waters; acidulous waters are those which contain much free carbonic acid; alkaline waters contain carbonate of potash, or of soda; and saline waters are such as contain neutral salts, generally sea-salt, and sulphate of magnesia, or Epsom salt.

In some districts, especially those of extinct volcanoes, waters occur combining the saline, the acidulous, and even the chalybeate characters. Thus at Nauheim in Hessa, there are numerous springs, used both as baths and for the manufacture

of the sea-salt they contain. But besides sea-salt, these springs contain also a large amount of carbonates of lime, magnesia; and iron, dissolved in a large excess of carbonic acid. As the acid escapes, these carbonates are deposited in the form of a hard stony mass, while the salt remains in solution. The springs rise from various depths, and, as is always the case, those whose source is deepest have the highest temperature. One of these, from a depth of between 400 and 500 feet, has a temperature but little below  $100^{\circ}$  F., and being charged with carbonic acid under this enormous pressure, when it issues from the tube, the gas forces it up in a perpetually flowing column of water, as thick as a man's thigh, and 18 feet high. Another, first obtained by boring in May, 1855, comes from a depth of 615 feet, and has a temperature of  $104^{\circ}$  F. It forms a perpetual jet 58 feet in height, and not much less in diameter than the other. The first contains upwards of 3.5 per cent., the latter rather more than 4 per cent. of sea-salt. This is quite as much as is present in sea water, which contains about 4 per cent. of saline matter, including chloride of potassium, chloride of magnesium, and carbonate of lime, besides sea-salt or chloride of sodium. There are no objects in Europe more curious or interesting than these fountains of Nauheim. A somewhat similar spring exists at Kissingen in Bavaria, but the jet is there intermittent.

The only way to obtain perfectly pure water, is to distil it; and in the laboratory, no water except distilled water should ever be used, provided distilled water can be procured in sufficient quantity. The process of distillation may be conducted on the small scale, as shown in the figure.



Water is the standard of specific gravity for liquid and solid bodies, and its specific gravity is therefore represented by 1.

Specific gravity or density is the term used to express the relative weights of different bodies ; that is, the compared weights of equal bulks. For equal bulks different bodies possess different weights ; one is heavier or more dense than another. In order to compare them in this respect, they are referred to water as a standard. Wood floats in water because a cubic inch of wood is lighter than a cubic inch of water. Lead sinks in water for the opposite reason.

To find the density, or specific gravity of a solid body, it is first weighed in air, and then in water. In the latter case it is lighter, and that by precisely the weight of its own volume of water, which it displaces when sinking in that fluid. Hence, if we subtract the weight in water from that in air, we obtain the weight of a quantity of water equal in bulk to the solid. If a bit of lead weigh in air 550 grains, it will be found, when weighed in water, to be lighter, and only to weigh about 500 grains. Subtracting 500 from 550, we have 50 grains as the weight of a portion of water exactly equal in bulk to 550 grains of lead. Now, water being the standard of Sp. G. for solids and liquids, we say  $50 : 550 :: 1 : 11$ , and we call the Sp. G. of lead 11, that of water being 1 ; or we say that lead is 11 times more dense than water.

To find the Sp. G. of a liquid, we generally use a bottle holding exactly 1000 grains of water when full, and having filled it with the liquid in question, find the weight of that liquid, which is necessarily of equal volume with the water. If we fill it with oil of vitriol, we find that it holds 1840 grains of that liquid ; so that if the Sp. G. of water be  $= 1$ , that of oil of vitriol will be 1.840, and if we call that of water 1000, that of oil of vitriol will be 1840.

Another method is to use the instrument called a hydrometer, which is formed of a hollow tube with a scale attached to it. In water, it sinks down till the liquid stands at the top of the scale, which is graduated downwards, and in heavier liquids it sinks proportionally less, so that we can read the Sp. G. on the scale. For lighter liquids, a hydrometer is made which only sinks to the bottom of the scale in water, and of course sinks deeper in lighter fluids such as alcohol and ether. Here the scale is graduated in a diminishing series towards the top of the instrument, beginning at 1000 and going on to 600, as no liquid is lighter than this. The scale for heavy liquids is graduated from 1000 to 2000.

A third plan is to use hollow beads, carefully prepared to float without sinking or rising in liquids, having the Sp. G. marked on the beads. When we have them, the beads are very con-

venient ; but they are troublesome to make. On the whole, for practical purposes, the hydrometer is the most useful instrument.

Gases are so much lighter than solids or liquids, that it would be inconvenient to use water as the standard for their Sp. G. Air is therefore taken for a standard, and the weight of a given volume of any gas is directly compared with that of the same volume of air ; exactly as with liquids, using a larger vessel. The method will be explained more fully when treating of air.

b. Deutoxide of Hydrogen.  $\text{HO}_2 = 17$ .

This compound is formed, in some cases, where oxygen is presented in the nascent state to water. The best process is that of Pelouze, which consists in adding to diluted hydrofluoric acid (fluosilicic or phosphoric acids may equally be used), kept very cold, exactly so much of the peroxide of barium, that neither barium nor the acid can be detected in the liquid, the whole of both being precipitated as fluoride of barium :  $\text{BaO}_2 + \text{HF} = \text{BaF} + \text{HO}_2$ . The deutoxide of hydrogen is dissolved by the surrounding water, and the filtered liquid is concentrated by being placed under the exhausted receiver, along with a vessel containing sulphuric acid, the whole being kept cold. The process, even in this form, is tedious and difficult, but much less so than the original method of Thénard, who discovered the compound.

The deutoxide, peroxide, or superoxide of hydrogen, when as free from water as possible, is a syrupy liquid, colourless, and possessed of a slightly disagreeable odour, like that of bleaching liquor, and of a peculiar, nauseous, bitter, and astringent taste. Its Sp. G. is 1.453 (water = 1). It does not become solid, even in a very intense cold.

This compound is very easily decomposed, yielding water and oxygen. The contact of carbon, of many metals, and even of metallic oxides, also of many salts, causes the separation of oxygen, often with explosion, and sometimes with a flash of light. It is very remarkable that peroxide of manganese, for example, should cause this rapid decomposition, without combining with any part of the disengaged oxygen ; and still more astonishing, that oxide of silver should decompose it with explosion, while the oxide of silver, so far from combining with more oxygen, loses all that is previously contained, and is reduced to the metallic state. We cannot, at present, explain these phenomena. The application of heat to the deutoxide of hydrogen, causes oxygen to escape with effervescence. It is less easily decomposed when diluted, and especially if acidulated ; the presence of a base, on the contrary, hastens its decomposition.

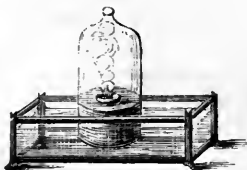


It is very probable that this remarkable compound will be found to possess valuable properties as a medicinal agent, and it is much to be desired that its preparation could be rendered easier.

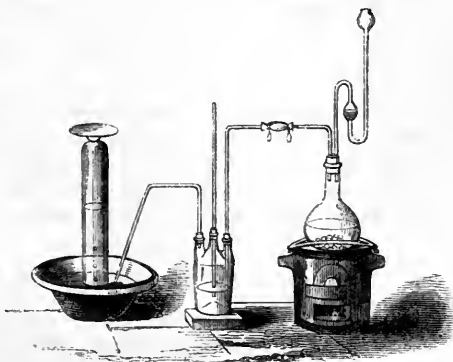
### 3. NITROGEN. $N=14$ .

**SYN. Azote.**—Discovered by Rutherford, in 1772. Occurs principally in the atmosphere, of which it forms 79 or 80 parts in 100 by volume, and about 77 by weight; also, in minute quantity, in the atmosphere as ammonia. It is an essential ingredient of all animal tissues, and of all such vegetable products as can be converted into blood in the animal body; also of the vegetable bases and other vegetable compounds, such as indigo, &c. &c.

It is easily obtained by the action of burning phosphorus on a confined portion of air, over water, as represented by the figure. The phosphorus takes the oxygen, forming phosphoric acid, which is soon removed by the water, and nitrogen gas is left.



It may also be obtained by causing a current of chlorine gas to pass through a solution of ammonia, in an apparatus such as is shown in the figure. Ammonia is composed of 1 eq. of nitrogen and 3 eqs. of hydrogen, and its symbol is  $NH_3$ . The change is as follows— $4 NH_3 + Cl_3 = 3 (NH_3, HCl) + N$ . That is, the 3 eqs. of hydrogen of 1 eq. of ammonia combine with the 3 eqs. of chlorine, forming 3 eqs. of hydrochloric acid,  $HCl$ , which combine with the three remaining eqs. of ammonia, forming 3 eqs. of hydrochlorate of



ammonia, and the nitrogen, 1 eq. of the decomposed eq. of ammonia, is set free. This process requires caution, as it may happen that the chloride of nitrogen, a most dangerous explosive compound, is formed. Should heavy yellow oily drops

appear in the ammonia, the operation should be suspended, and the apparatus, after detaching the flask, left to itself till the chloride has been decomposed.

Perfectly pure nitrogen may be very easily prepared by heating a tolerably concentrated solution of hyponitrite of ammonia : the following equation represents the decomposition :



Nitrogen is a colourless and transparent gas, devoid of taste and smell, and chiefly distinguished by the absence of active properties. It does not support combustion, neither does it burn itself. It is incapable of supporting animal life, and consequently an animal, immersed in pure nitrogen, soon dies ; but only because oxygen is absent, for nitrogen itself is so far from being poisonous, that the air we breathe contains  $\frac{4}{5}$ ths of its bulk of that gas in an uncombined state. It serves to dilute the oxygen, and for that purpose it is admirably adapted, from the absence of marked characters, or strong affinities. Its specific gravity is rather less than that of air, being 0.9722 ; so that 100 cubic inches weigh about 30.12 grains.

Nitrogen cannot be made to unite directly with any element, and only forms combinations when one or both elements are in the nascent state. It is, therefore, unlike the other metalloids, in a high degree chemically indifferent or neutral. But, under favourable circumstances, it does combine with most of the metalloids, and with several metals. Its most important compounds are those with oxygen and with hydrogen. Almost all compounds of nitrogen are easily decomposed, and many of them are even dangerous, from their tendency to explode from very slight causes.

It is this very character of easy decomposability that gives to the compounds of nitrogen their very high importance in the organised kingdoms of nature. We shall hereafter see how important a part these compounds perform in the formation, as well as in the destruction, of organic bodies.

#### NITROGEN AND OXYGEN.

##### a. Atmospheric Air.

The air of our atmosphere is chiefly formed of nitrogen and oxygen, not in a state of combination, but simply mixed together. Dalton has shown that, when any two gases, however different in density, are placed in communication, they are very soon found to be completely and equally mixed, even although they have no tendency to combine chemically. This

is easily shown by placing a narrow-necked bottle full of hydrogen, with the mouth downwards, in connection with a similar bottle full of carbonic acid, the latter with its mouth upwards. Although hydrogen is about 21 times lighter than carbonic acid, and has no tendency to combine with it, yet, after a short time, we find hydrogen in the lower vessel, and carbonic acid in the upper one. The same thing is of course true of oxygen and nitrogen, which differ so little in density. The properties of each of the gases are present, only modified slightly by the presence of the other ; whereas chemical combination gives rise to new compounds, possessing entirely new properties. This is eminently the case in the compounds which are really formed between nitrogen and oxygen, so that we are forced to look upon the air as a mixture merely.

It is remarkable, however, that the proportions of the gases are such as correspond almost exactly, by weight and by volume, to 2 eq. of nitrogen and 1 eq. of oxygen. Of 100 vol. of air, 79 or 80 are nitrogen, and 20 or 21 oxygen. Here we have the ratio of 4 vol. to 1. 100 parts of air, by weight, contain nearly 77 of nitrogen and 23 of oxygen ; that is almost exactly 28 of nitrogen to 8 of oxygen, or  $N_2 O$ .

The physical properties of air are well known. It is, like all gases, elastic, and it possesses such a density that 100 cubic inches weigh about 31 grs. This is easily shown. A large and light Florence flask is fitted with a stopcock, and weighed, being, of course, full of air. The air is then removed from it by the air-pump, and it is again weighed. It is now lighter than before, and the difference is the weight of air it contained. It is easy to ascertain the volume of this air by measuring the quantity of mercury which enters the exhausted flask when opened under mercury. The mercury that enters is precisely equal in bulk to the air extracted, and even if the flask has been imperfectly exhausted, the experiment is good, for we learn from it the weight and the volume of a certain quantity of air. If the flask have the capacity of 100 cubic inches it will be found to hold about 31 grains of air ; if 50 cubic inches, 15·5 grains of air, and so on.

Hence, the whole atmosphere presses on the surface of the earth with a very great force, equal to about 15 lbs. on each square inch of surface. In other words, a column of air, 1 square inch in base, and equal in height to the atmosphere, weighs 15 lbs. But the further consideration of this subject belongs to physics. Air is made the standard of specific gravity for gases and vapours, and its Sp. G. is made 1·000. To find the Sp. G. of any gas, take the exhausted flask of the last

experiment (finding the weight of air), and, after connecting its stopcock with the stopcock of a jar full of the gas, open both stopcocks, when the gas rushes in to the empty flask, and soon fills it. It is now again weighed. Suppose it has been found to contain 20 grs. of air; if filled with chlorine, it will be found that the flask is 30 grains heavier than when full of air. Hence, the weight of a volume of chlorine equal to that of 20 grs. of air is  $20 + 30 = 50$  grs. But as air is the standard of the Sp. G. of gases, and its Sp. G. is made  $= 1.000$ , we have the following proportion:— $20 : 50 :: 1 : 2.500$ , and thus we obtain 2.500 for the Sp. G. of chlorine, and we see that this gas is twice and a half as dense as air.

When we wish to know the density of a vapour—that is, of the gas of a substance which is solid or liquid at ordinary temperatures—we place a certain portion of it in a light and accurately weighed flask, of which the neck is then drawn out to a small diameter. The substance is then boiled till all air is expelled by the vapour, which must issue in a full stream from the tube, till all superfluous matter is expelled, and the escape of vapour ceases, and then the tube is instantly sealed up by the flame of a spirit-lamp, the temperature of the flask at the moment, and the state of the barometer, being noted. The weight of the flask full of vapour is next taken at the ordinary temperature, when the substance is again liquid or solid, but this does not affect the weight of it. The weight of the flask full of air has been previously ascertained. The next thing is to measure its capacity, which is done by breaking the point of the tube under pure mercury, which rushes in and fills the flask. The mercury is then accurately measured in a graduated tube, and we thus find the volume of air and vapour contained in the flask.

But this volume has to be corrected to the normal temperature of  $60^{\circ}$ , and the normal pressure of 30 inches.

The correction for pressure is made according to this law, that gases expand for each degree of heat  $\frac{1}{460}$  of their bulk, as measured at  $0^{\circ}$ . That is, 460 volumes at  $0^{\circ}$  will be 461 at  $1^{\circ}$ , 470 at  $10^{\circ}$ , or 520 at  $60^{\circ}$ . If, then, we know the volume of the air in the flask at  $50^{\circ}$ , its volume at  $60^{\circ}$  is easily found, for 460 vol. at  $50^{\circ}$  would become 510; and as  $510 : 520 ::$  the volume of air at  $50^{\circ}$  to its volume at  $60^{\circ}$ .

The correction for pressure is very simple. The volume of a gas varies inversely as the pressure; so that if we measure a gas under the pressure of 29 inches, its volume will be larger than it would be at 30 inches, in the proportion of 30 to 29. Suppose its volume at 29 inches to be 20 cubic inches, then we

have : 30 : 29 :: 20 : 19·33, which is the true volume under 30 inches barometer.

Having thus ascertained the true volume of the air contained in the flask, we can easily calculate its weight, because we know that 100 cubic inches of air, at 60° and 30 inches, weigh 31·0117 grains. The weight of the air, thus calculated, being deducted from that of the flask full of air, gives the weight of the empty flask ; and this again, deducted from the weight of the flask full of vapour, gives us the weight of the vapour which accurately filled the flask when sealed.

We have now to find the volume of this vapour at the normal temperature and pressure. As the flask was sealed at a high temperature, say 200°, the vapour was in a very expanded state, and having at that temperature the volume of the air (supposed to be 20 cubic inches), would have a far smaller volume at 60°, if it could exist as vapour at that temperature. The correction is made by the rule above given ; that for pressure is added, and now, at last, we have the precise volume of a certain weight of the vapour of the substance, and can compare this weight with that of an equal volume of air, and thus learn its specific gravity in the gaseous form.

The chemical properties of air are chiefly those of the oxygen it contains, modified by the presence of 4 times its bulk of the negative body, nitrogen. Air supports combustion, and the respiration of animals, as long as the proportion of oxygen does not fall below a certain amount.

Besides nitrogen and oxygen, the air always contains more or less watery vapour, which is almost equally important to animal and vegetable life, since neither animals nor plants can live long in a perfectly dry air.

Air also contains, as ingredients essential to the life of plants, and thus indirectly also to that of animals, minute proportions of carbonic acid and of ammonia. The amount of the former seldom in the open air exceeds  $\frac{1}{1000}$  part of the weight of the air ; while the proportion of ammonia is much smaller even than this.

When it is required to ascertain the exact proportion of oxygen in any specimen of air, the object may be attained in a variety of ways. The operation is called eudiometry, and the instruments employed, eudiometers. The most commonly employed is that of Volta, modified by Ure, which is simply a graduated glass tube, closed at one end, bent as in the figure, and furnished with two platinum wires, to allow the electric spark to pass. The air being introduced and measured, half its bulk of pure hydrogen gas, or thereabouts, is added, and the whole measured again. The gas being confined by water or

mercury,' and the open end of the tube stopped by the finger or thumb, the spark is passed through the mixture, when an explosion takes place, and a certain portion of the mixture dis-



appears, the water or mercury rising in the tube to supply its place. The residue is now measured, and  $\frac{1}{2}$  of the volume which has disappeared is oxygen. It is obvious that, if there be enough of hydrogen, the whole of the oxygen will assume the form of water, and both the oxygen and hydrogen of that water must lose the gaseous form. Now, as water is formed of 2 vol. of hydrogen to 1 vol. of oxygen,  $\frac{1}{3}$  of the volume of the gases which have combined must be oxygen.

If, for example, 100 measures of air are mixed with 50 of hydrogen, the bulk of the whole will be 150. If, now, after explosion, 87 parts remain, it is plain that 63 have disappeared, and of these 63 measures 21, or  $\frac{1}{3}$ , are oxygen, originally contained in the 100 of air, while 42, or  $\frac{2}{3}$ , are hydrogen.

Gay-Lussac has lately proposed to remove the oxygen from a measured portion of air by means of copper moistened by sulphuric or hydrochloric acid, which soon absorbs that gas completely. The diminution of volume here is exactly equal to the proportion of oxygen present.

There are many other eudiometrical methods, but the above are the best.

The amount of water in the atmosphere is ascertained by hygrometers, of which there are various kinds. That of Daniell is the best. It is founded on the fact, that the temperature at which the water contained in the air is deposited as moisture, varies with the amount of moisture present. The drier the air, the more must it be cooled before it begins to deposit moisture. If the air be saturated with moisture, the cooling of it one degree will cause a deposition of dew: the temperature at which dew is deposited is called the dew-point. The details of this and other hygrometers belong to physics.

The presence of water in the atmosphere may be shown at any time by exposing a deliquescent substance, such as chloride of calcium, to the air, when it quickly becomes moist and finally liquifies by attracting moisture. Air, or any other gas, may thus be dried, either in a tube over mercury, into which the drying substance is introduced, or by passing the gas through a long tube filled with the substance in coarse powder, or through strong sulphuric acid, which has a powerful affinity for water,

or, as is often done, through U-shaped tubes, filled with pumice-stone moistened with sulphuric acid.

The uses of atmospheric air are obvious. Besides supporting animal and vegetable life, it is essential to all our modes of obtaining heat and light by combustion, and it is equally indispensable to eremacausis, or the decay of dead organic matters, which is, in fact, a slow combustion.

There is reason to think, that ozone plays an important part in the process of eremacausis or decay. It appears that when certain oxidisable organic substances are exposed to air, ozone is produced, just as when phosphorus is thus exposed. Now, dead animal or vegetable matter, more especially when putrescent, yields highly oxidisable products, which may probably cause the formation of ozone, even if that substance were not naturally formed in the air by electricity. When formed, it probably commences the eremacausis, which, once begun, goes on in the same way as combustion. And the use of ozone is, probably, by thus assisting in the process of decay, to promote the resolution into gaseous forms of dead organic matter, which would otherwise accumulate so as to render the earth uninhabitable.

We may here consider also the process of spontaneous combustion, which frequently takes place in finely divided charcoal, such as is prepared for the manufacture of gunpowder, and also in porous matters, such as tow or cotton, when used for wiping machinery, and thus moistened with oil. These substances first enter into eremacausis, or slow combustion, in which but little heat and no light is produced. But the warmth evolved hastens the process; the temperature rises still more; the oxidation is still more accelerated, till at last a spark appears, which finally bursts into flame. It is almost certain that ozone is concerned, at least in the commencement of the process, which is simply eremacausis.

Spontaneous combustion may be beautifully demonstrated by the following experiment. A few drops of a solution of phosphorus in bi-sulphide of carbon are dropped on a small sheet of filtering paper, on which the solution spreads, and instantly dries up, leaving phosphorus as a finely divided white powder. The paper is placed on a ring, to facilitate access of air. The phosphorus immediately begins to undergo slow combustion, is luminous in the dark, and gives off thin white vapours. Now we know that ozone is formed in contact with phosphorus, and afterwards oxidises it. By degrees the vapours increase and the temperature rises, for after a few minutes, the phosphorus all at once bursts out into vivid combustion. We can hardly

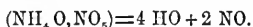
doubt that the spontaneous combustion of finely divided charcoal, as well as of porous organic matters moistened with oil, depends on the same causes.

It is very important to remark, that although the processes of respiration and combustion, as well as that of the decay and putrefaction of animal and vegetable matter, are constantly removing oxygen from the air, yet the proportion of that element never diminishes, being kept up by the process of vegetable life. In like manner, respiration and combustion are continually sending carbonic acid into the atmosphere in place of the oxygen they consume, and yet the air does not become more highly charged with carbonic acid; for the same process of vegetable life which restores oxygen to the air, removes an equal bulk of carbonic acid,—from which, indeed, the oxygen thus restored is derived.

Plants are constantly absorbing carbonic acid from the air, and indeed obtain the whole of the large amount of carbon they contain from this source. But under the influence of light, their leaves are as constantly decomposing the carbonic acid, and setting free its oxygen, which is equal in volume to the carbonic acid. Animals, on the contrary, take up oxygen, and give out carbonic acid, and there is a perfect balance between the opposite processes of animal and vegetable life.

b. Protoxide of Nitrogen.  $\text{NO} = 22$ .

*SYN. Nitrous Oxide; Intoxicating or Laughing Gas.*—Prepared by applying a moderate heat to pure nitrate of ammonia in a retort. The salt melts, boils, and is soon entirely volatilised in the form of water, which trickles down the neck of the retort, and protoxide of nitrogen, which being gaseous may be collected over water. The following equation represents the change:



Showing that 1 eq. of oxide of ammonium and 1 eq. of nitric acid yield 4 eq. of water, and 2 eq. of protoxide of nitrogen.

This compound is a gas, colourless and transparent. It has a faint smell and a sweetish taste. It is slowly absorbed by water, and therefore cannot be long kept over that liquid. Its specific gravity is 1.527. It may be liquefied by a pressure of 56 atmospheres.

By weight it contains 8 parts of oxygen to 14 of nitrogen, and by volume, 2 vol. of nitrogen and 1 vol. of oxygen, condensed into the bulk of 2 vol. Hence the great density of the gas, which contains its own bulk of nitrogen, and half its bulk of oxygen, while air only contains  $\frac{1}{5}$  of its bulk of that gas. Con-



sequently, as some combustible bodies, such as phosphorus, or a candle, if burning, are capable of decomposing this gas, and seizing its oxygen, they burn in it with great brilliancy. Probably for a similar reason it is capable of supporting life for a short time, if respired, and its action on the human system is most remarkable. In most persons it causes very agreeable sensations, a sense of lightness, a rapid and brilliant flow of ideas, accompanied with an irresistible tendency to laughter, and to very violent muscular exertion. These effects only last for a minute or two after the gas has been breathed as much as possible: but they are not followed, like those of other excitants, by any sense of depression or languor: on the contrary, a certain feeling of exhilaration and unusual lightness of spirits is often felt for a whole day after. In some cases the effects are unpleasant, such as head-ache, a rush of blood to the head, and a tendency to stupor. The experiment must therefore be made with caution, and the gas withdrawn, should the face of the experimenter appear flushed to any considerable extent. As he is often, however, unwilling to relinquish the bag of gas, an aperture should be made in the side of the breathing-pipe, and stopped with a cork, which may be removed if necessary, thus admitting air to the mouth, and putting an end to all danger. These very singular properties of this gas were first discovered by Davy; and in a physiological point of view, they merit further investigation than they have yet received. The gas has been tried in medicine, but hitherto without much benefit: although in America it is said to have been found useful in cases of melancholia.

Since the discovery of the anæsthetic effects of ether and chloroform, the nitrous oxide has again attracted the attention of medical men. Indeed, it was originally noticed by Davy and Gilbert that the gas appeared to produce insensibility to pain, but this point was not investigated. In America it is understood that the anæsthetic effects of ether were observed by Morton, after he had tried to use nitrous oxide in the same way. One thing is very certain, namely, that all who have inhaled the three substances perceive an exact similarity in the sensations, as long as they are conscious. I myself can perceive no difference whatever. It is true that the nitrous oxide generally causes laughter, excitement, and violent muscular efforts, while ether and chloroform usually soon induce stupor, and at least quietness. But the chief cause of this difference is that from the gaseous form of the nitrous oxide we cannot give a full dose of it in most cases. It must be breathed from a bag, through a tube, and very soon, before the period of stupor arrives, the muscles of

the lips are relaxed, and air entering, cuts short the experiment in the stage of excitement.

But, having administered the gas to several hundred persons, I have often seen them pass this first stage, and fall into a state quite the same as that produced by chloroform. Nay, I have satisfied myself that insensibility to pain existed, and, indeed, it often appears in the excited, or early stage. I lately saw a gentleman strike repeatedly with his closed hand, and with prodigious force, against a skirting of wood, so as to bruise his hand very severely, and it was only as the excitement passed off that he was led to look at his hand, and was astonished to see it covered with blood. However this may be, the gas now and then produces the advanced stage, or that of stupor, and in that case, complete anæsthesia for the time.

On the other hand, when ether or chloroform is carelessly administered, and too little inhaled, the results frequently stop at the stage of excitement, precisely as with nitrous oxide. In short, the perfect similarity of the sensations produced when these different substances are inhaled, and the occasional occurrence of the very same results in both cases, such as of anæsthesia from nitrous oxide, and of excitement from ether or chloroform, lead to the conclusion that the action of all is the same, or at least of the same kind, and that it is the difference of form which causes the usual difference of results, since it must be very difficult, with a gas, to pass beyond the first stage, the gas requiring a voluntary exertion to inhale it through a tube, while a patient may be made to inhale the vapour of ether or of chloroform, without any effort on his part, till the full effect is produced. It is to be remembered that in many cases nitrous oxide causes no excitement, but only stupor, and in many of these the appearances are exactly those produced by chloroform.

But, although I believe that this gas has anæsthetic properties, and that to a high degree, I do not think it can ever be used in surgery, from the mechanical difficulty above alluded to, which, indeed, is probably the reason why its anæsthetic effects were not long ago observed. Those who inhaled it rarely got beyond the first or excited stage, which attracted attention exclusively.

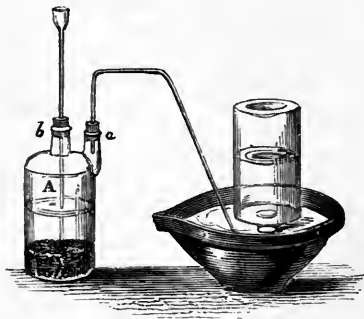
Protoxide of nitrogen is neutral or indifferent, and has hardly any tendency to combine with other bodies. According to Pelouze, however, it combines with the salts of sulphurous acid, or sulphites.

c. Deutoxide of Nitrogen.  $\text{NO}_2 = 30$ .

*Syn. Nitric Oxide: Nitrous Gas.*—Best obtained by the action of copper clippings on moderately strong nitric acid, in the appa-

ratus figured. The metal is dissolved with effervescence, and the gas may be collected and preserved over water. The action is as follows:  $\text{Cu}_3 + 4 \text{NO}_5 = 3 (\text{CuO}, \text{NO}_5) + \text{NO}_2$ . The gas escapes, and nitrate of copper is left in the bottle.

A gas, transparent and colourless. Its taste and smell are not known, because as soon as it comes in contact with air, it forms, with the oxygen, red vapours of nitrous acid, which have a suffocating smell, and a rough, acid, corrosive taste. It supports, like the preceding gas, the combustion of burning phosphorus, and for the same reason, namely, that it contains half its bulk of oxygen, being formed of equal volumes of nitrogen and oxygen, united without condensation. Its specific gravity is consequently the mean between those of oxygen and nitrogen, or 1.0416. A burning candle is extinguished in this gas, and it not only does not support life, but cannot be breathed, as it forms nitrous acid gas in the mouth, and the glottis instinctively closes against the latter.



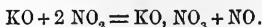
Its most distinctive character is that of forming, when mixed with air or oxygen, a red gas or vapour, which is nitrous acid, and which instantly disappears if in contact with water, being absorbed by that liquid. As the formula of the deutoxide is  $\text{NO}_2$ , and that of nitrous acid,  $\text{NO}_4$ , it is plain that the latter may be formed from the former by the mere addition of oxygen. As the red vapours are very remarkable, the deutoxide may be used as a test of the presence of free oxygen in a gaseous mixture.

If a few drops of bisulphuret of carbon be added to a jar of this gas, and a light applied to the mixture, it burns rapidly with a bright blue flash of light.

The deutoxide of nitrogen is abundantly absorbed by any solution containing a salt of protoxide of iron, such as green vitriol, forming a brown solution, from which the gas may be expelled unchanged by boiling. This solution absorbs oxygen, and has been used in eudiometry, but it does not give accurate results.

d. Hyponitrous Acid.  $\text{NO}_3 = 38$ .

SYN. *Acide Nitreux* ; *Salpetrige Säure*.—It is formed when a strong base, such as potash, is brought into contact with the preceding gas, protoxide of nitrogen being given off, while the acid unites with the base. Thus,



It is best obtained, however, by heating 1 part of starch in 8 parts of nitric acid, Sp. G. 1.25, and conducting the disengaged gases, first through a long tube filled with chloride of calcium, to remove water, and then through a dry tube cooled down to  $-4^\circ \text{F}$ . in which latter the acid condenses, as a very volatile liquid which, while cold, is colourless, but at the ordinary temperature becomes green. Its properties are little known.

In contact with water it is destroyed, giving rise to nitric acid and deutoxide of nitrogen, thus :

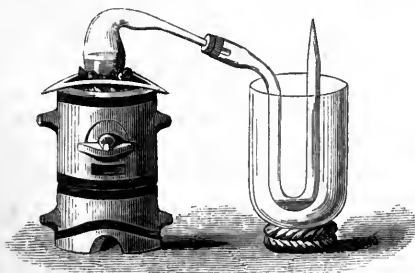


The salts of this acid are obtained by heating a nitrate,—for example, nitrate of potash or soda,—till it begins to precipitate nitrate of silver brown. The whole is then precipitated by nitrate of silver, the precipitate dissolved in boiling water, and the hyponitrite of silver crystallises on cooling. From this salt by the action of soluble chlorides, the other hyponitrites may be obtained. They have been little studied.

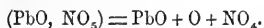
e. Nitrous Acid.  $\text{NO}_2 = 46$ .

SYN. *Acide Hyponitrique*. *Untersalpetersäure*.—This is the

acid which appears as red vapours when deutoxide of nitrogen mixes with air, or with oxygen. 1 vol. of deutoxide of nitrogen, and  $\frac{1}{2}$  vol. of oxygen, if mixed quite dry, and cooled, form the liquid nitrous acid ;



but it is most easily obtained by distilling dry nitrate of lead, as in the figure. Equation,



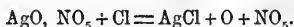
In this experiment oxide of lead is left, and oxygen gas and

nitrous acid pass over, the latter condensing in the well-cooled receiver. If intensely cold, it is colourless; but as it becomes warmer, it assumes a yellow or orange colour. Its Sp. G. in the liquid form is 1.42. It boils at about  $82^{\circ}$ , and is converted into a deep red vapour, or gas, which, if further heated, becomes nearly black, or impervious to light. If once mixed with air or any other gas, it can only with very great difficulty be condensed, so that it is commonly seen in the form of vapour. It has an unpleasant suffocating smell, and cannot be breathed with impunity even for a moment. It supports the combustion of almost all combustible bodies, by virtue of its large proportion of oxygen.

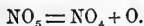
In contact with water, it is destroyed, giving rise, like the preceding acid, to nitric acid, and deutoxide of nitrogen. Thus,  $3\text{NO}_4 = 2\text{NO}_5 + \text{NO}_2$ . As it undergoes the same change in contact with all bases hitherto tried, its salts are unknown. Along with pure nitric acid, it forms the orange-fuming nitric acid of the shops, often called nitrous acid. It has lately been observed, that if 2 vol. of deutoxide of nitrogen, and 1 vol. of oxygen, both absolutely dry, be made to pass through a tube cooled to  $0^{\circ}$ , and also quite dry, nitrous acid is obtained in the form of prismatic crystals. These may also be obtained by collecting separately, in a dry tube at  $0^{\circ}$ , the latter products of the distillation of nitrate of lead. They melt at  $16^{\circ}$ , and cannot be again solidified. Even at  $0^{\circ}$  the slightest trace of water causes the nitrous acid to assume the liquid form.

f. Nitric Acid.  $\text{NO}_5 = 54$ .

Till recently nothing was known of this compound, and the strongest and dryest nitric acid we could obtain was the hydrated acid, to be presently described. To obtain it, perfectly dry nitrate of silver is exposed to the action of a current of chlorine gas at the temperature of  $140^{\circ}$  in an apparatus from which all cork, caoutchouc, or other organic matter, is excluded. Chloride of silver is formed, oxygen gas is given off, and volatile prismatic crystals are formed, which are anhydrous nitric acid; as we see by the equation



It melts at  $85^{\circ}$  or  $86^{\circ}$  and boils at  $112^{\circ}$ , and if heated a little further is decomposed, yielding nitrous acid and oxygen.



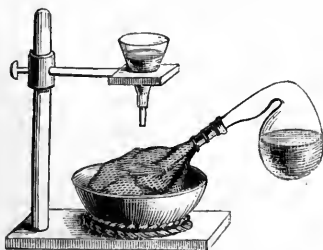
just as happens when it is expelled from nitrate of lead by heat. It is instantly converted by water into the hydrated acid. In

fact, we have no certainty that the body  $\text{NO}_5$  is an acid at all, for we cannot test it without bringing it into contact with water, or with bases, both of which change it. And at all events, as in most other cases, the true acid is the hydrated acid, in all probability because the presence of replaceable hydrogen is an essential character of all powerful acids.

Formula of the hydrated acid,  $\text{HO}, \text{NO}_5$ , or  $\text{H}, \text{NO}_6 = 63$ .

This, the most important of all the compounds of nitrogen and oxygen, occurs very frequently in nature, chiefly combined with potash or soda, forming nitre and cubic nitre; also in minute proportion in rain-water after thunder-storms. It is formed in natural or artificial nitre beds, where animal or vegetable matter containing nitrogen is exposed to the air along with bases. The nitrogen being disengaged as ammonia,  $\text{NH}_3$ , is oxidised along with the hydrogen, yielding nitric acid and water; thus  $\text{NH}_3 + \text{O}_2 = \text{NO}_5 + 3 \text{HO}$ . The acid is seized by the base present, and nitre is formed.

The hydrated acid,  $\text{HO}, \text{NO}_5$ , or  $\text{H}, \text{NO}_6$ , is the substance commonly called nitric acid. It is best prepared by the distillation of a mixture of equal weights of hydrated sulphuric acid, or oil of vitriol, and of nitre or saltpetre, the nitrate of potash. The salt in coarse powder being introduced into a plain retort, the acid is poured in by means of a retort funnel. The retort is then placed in a sand-bath over the lamp, and cautiously heated, till the acid begins to drop into the receiver, which is to be surrounded with cold water. As the nitre generally contains a little sea-salt, the first portions of acid which distil are impure, containing chlorine, and nitrous acid; but they serve to wash quite clean the neck of the retort: on which some sulphuric acid is

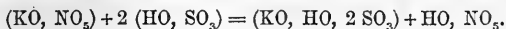


commonly to be found, in spite of all our care, as well as traces of the powdered nitre. It is best, therefore, to collect the first portion, say  $\frac{1}{10}$ th of the whole, in a separate receiver, and when the liquid that drops is found to be free from chlorine (by the test of nitrate of silver), the receiver is changed, and

the rest of the nitric acid is thus obtained quite pure, or at most, slightly tinged by nitrous acid. By this simple device, we avoid the necessity of re-distilling the acid, as commonly directed. The impure portion which first passes over, is ex-

tremely well adapted for all experiments of illustration, and ought to be carefully preserved for such purposes.

The following equation explains the change in this process :—



For 1 eq. of nitre, we take 2 eq. of oil of vitriol, and we obtain 1 eq. of hydrated bisulphate of potash, and 1 eq. of hydrated nitric acid. We take equal weights of the materials, because 1 eq. of nitre weighs 102, while 2 eq. of oil of vitriol weigh 98; and a slight excess of the latter is advantageous rather than otherwise. By using 1 eq. of oil of vitriol, we may also obtain nitric acid; but a much higher temperature is required, and a large part of the acid is decomposed into oxygen, which escapes, and nitrous acid, which combines with the nitric acid, giving it a deep-red colour, and causing it to give out red fumes. Moreover, in the latter case, neutral sulphate of potash is left, which can hardly be got out of the retort without breaking it; while the bisulphate of potash, formed in the operation first described, may be easily dissolved out by hot water.

Hydrated nitric acid, when pure, is a colourless liquid, giving out dense gray fumes, on exposure to the air. Its Sp. G. is 1.52 to 1.53. It freezes at  $-40^\circ$ , and boils at  $186^\circ$ . If diluted somewhat with water, so as to have the Sp. G. 1.424, it boils at  $248^\circ$ ; but if still weaker, it boils more easily, and becomes stronger, till the boiling point reaches  $248^\circ$ , when it distils over unchanged. It is then a second hydrate, the most stable of the two, the formula being  $NO_3, 4 HO$ . Nitric acid has a pungent, rather disagreeable smell, is very acid and corrosive, and stains the skin, and organic matter in general, yellow.

It has a strong attraction for water, and becomes hot when mixed with it. (Acid of middling strength, mixed with snow, causes it to liquefy instantly, producing intense cold.)

Nitric acid is very easily decomposed. If passed through a red-hot porcelain tube, it is resolved into oxygen and nitrogen. All combustible or oxidisable bodies deprive it of oxygen, reducing it to nitrous acid, hyponitrous acid, or deutoxide of nitrogen; and even, in some cases, removing all the oxygen, and leaving only nitrogen gas. The action is generally attended with heat; and in some cases as with phosphorus and essential oils, combustion takes place, and even dangerous consequences may ensue from the acid, or the burning body, which is scattered about by the violent commotion. Nitric acid is, therefore, a very powerful oxidising agent, and is much used for oxidising and dissolving metals, such as silver, copper, mercury, &c. It is remarkable that the very strongest acid does not attack

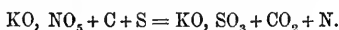
metals ; but, on the addition of a few drops of water, a most violent action ensues.

The presence of nitric acid in a liquid is best ascertained by adding pure oil of vitriol, and then a drop or two of solution of green vitriol. If nitric acid be present, a red or brown colour will appear where the two liquids meet : and by this test  $\frac{1}{24000}$  of nitric acid may be detected.

Pure nitric acid ought to be entirely volatile ; and when diluted with distilled water, to give no precipitate with the salts of baryta, or of silver.

Nitric acid is used in medicine, and in the arts ; in the latter, as aqua fortis. To the chemist, it is one of the most valuable agents, and is daily employed as a means of oxidising metals and organic substances. The tendency of this acid to yield oxygen to combustible bodies is found also in its salts, especially at a red-heat ; and hence, nitrate of potash, or saltpetre, is an essential ingredient of gunpowder, and of the various mixtures used for rockets and fireworks ; in all of which it is mixed with charcoal and sulphur.

The principle of the composition of gunpowder is as follows. Charcoal or carbon, and sulphur, both combine with oxygen to form gaseous compounds, and at a red-heat they take this oxygen from the nitric acid of the saltpetre. At the same time the nitric acid, by losing a part or the whole of its oxygen, also yields gaseous products, and thus, from a solid of small bulk, there is instantaneously produced a volume of gases many hundred times greater than that of the solid even at ordinary temperatures, but much expanded by the red-heat of the action. Hence the prodigious elastic force of gunpowder. If we suppose 1 eq. of nitre, 1 of charcoal, and 1 of sulphur, we should have



Here the sulphur is converted into the sulphuric acid, which combines with the potash, while carbonic acid and nitrogen gases are given off at a red-heat. In practice, sulphurous acid gas is also given off, and sulphuret of potassium is formed at least in part, but the principle is that here explained. The actual proportions employed are varied according to the quality of powder desired. That used in the army contains 75 per cent. of saltpetre, 10 per cent. of sulphur, and 15 per cent. of charcoal. Fine powder contains 76·9 of saltpetre, 9·6 of sulphur, and 13·5 of charcoal per cent.

With bases, nitric acid forms salts called nitrates. Most of these are neutral, with the general formula  $\text{MO}, \text{NO}_3$  ; but there



are a few basic nitrates, in which one or more atoms of the base are added to the neutral salts. All the nitrates are decomposed by sulphuric acid, and they may be recognised by deflagrating with red-hot charcoal, and by the test above given for nitric acid, which distinguishes them from other deflagrating salts, such as chlorates, &c.

#### NITROGEN AND HYDROGEN.

These elements do not combine directly, but only when one or both are in the nascent state, as in the decomposition of substances containing them, such as animal or vegetable matters, by heat, fermentation, or putrefaction. They are believed to form three compounds, amide, or amidogen, ammonia, and ammonium, of which ammonia alone is known in the separate state.

##### a. Amide. $\text{NH}_2 = 16$ .

**SYN. Amidogen.**—This compound is unknown in a separate state, but is believed, with some reason, to exist in many compounds. If potassium, for example, be heated in dry ammoniacal gas,  $\text{NH}_3$ ,  $\frac{1}{3}$  of the hydrogen is expelled, and an olive-coloured solid remains, the composition of which is  $\text{K}, \text{NH}_2$ . It is viewed as a compound of potassium with amide, the amidide or amiduret of potassium. When put into water, potash and ammonia are formed, thus,  $\text{K}, \text{NH}_2 + \text{HO} = \text{KO} + \text{NH}_3$ . Compounds of amide with sodium, with various other metals, with carbonic oxide (oxamide), with benzoyle (benzamide), and other substances, are known. But these bodies are now generally considered to be ammonias, in which 1 eq. of hydrogen has been replaced by a metal or radical. The so-called amidide of potassium, for instance, is ammonia in which potassium has been substituted for 1 eq. of the hydrogen. The compound in which all the hydrogen of ammonia has been so replaced,  $\text{NK}_3$ , is also known. Their general character is, in contact with water, and under the influence of acids and bases, to be resolved into ammonia and an oxidised product, commonly an acid. Thus oxamide,  $\text{C}_4\text{O}_4, 2\text{NH}_2$ , along with water,  $4\text{HO}$ , in the presence of an acid or an alkali, yields oxalate of ammonia,  $\text{C}_4\text{O}_6, 2\text{NH}_4\text{O}$ . It is this very powerful affinity for hydrogen which has hitherto defeated all our efforts to isolate amide. The various compounds of amide will be described in their proper order.

##### b. Ammonia. $\text{NH}_3 = 17$ .

**SYN. Volatile alkali.**—Occurs in combination with hydrochloric acid, as sal-ammoniac; in the urine of animals, especially

of birds and reptiles, as urate of ammonia ; in aluminous and ferruginous rocks and earths in small quantity ; finally, in the air, as a constant result of the putrefaction, decay, or combustion of organic matters containing nitrogen.

It is formed abundantly in putrid urine (from urea), and in the destructive distillation of organic nitrogenised matter, as, in Egypt, by heating camel's dung ; in Europe, formerly, by distilling horn (hence the name spirit of hartshorn), at present by distilling any animal refuse ; or in the distillation of coal in gas-works, which yields abundance of ammonia. In all these cases it is found as carbonate, and in the soot of coal as sulphate.

To obtain ammonia, powdered sal-ammoniac is mixed with about an equal weight of dry hydrate of lime (slacked lime), and the mixture heated in a retort, or a flask fitted with a bent tube. The ammoniacal gas is abundantly disengaged, and may be collected over mercury, or, as it is much lighter than air, by displacement, the tube being made to reach, as in the cut, to the closed end of the gas-receiver, the open end being downwards. A large tube or vessel may be easily filled with the gas in this way, and preserved by immersing the open end, when filled, in a small cup of mercury. The following equation represents the change in its production.  $(\text{NH}_3, \text{HCl}) + (\text{CaO}, \text{HO}) = \text{CaCl} + 2 \text{HO} + \text{NH}_3$ .

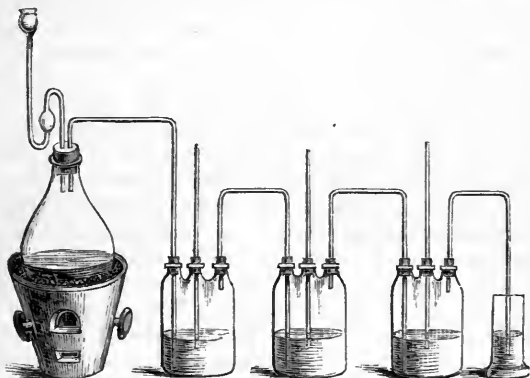


Ammonia is a gas, transparent and colourless, of a very pungent and peculiar smell and taste. It is liquefied by a cold of  $40^\circ$ , or by a pressure of about 7 atmospheres ; and by a very intense cold, it is frozen to a white crystalline mass. It is instantly absorbed by water, forming that solution of the gas called aqua or liquor ammoniæ. It extinguishes a candle, does not burn itself under ordinary circumstances, and, if respired undiluted, is fatal to animal life. Its Sp. G. is 0.5902, being thus little more than one-half as heavy as air. It possesses strong alkaline or basic properties, neutralising the strongest acids. The approach of any gaseous or volatile acid, such as carbonic, hydrochloric, or nitric acids, to the mouth of a jar of ammonia, causes the formation of dense white clouds of carbonate, hydrochlorate, or nitrate of ammonia. By this property and by its smell, it is easily detected and recognised. If the ammonia be combined with an acid, it must be set free by the addition of lime or potash before these tests can be applied.

Ammonia is formed by the union of 3 vol. of hydrogen and 1 vol. of nitrogen, which yield not 4 vol. but 2 vol. of ammoniacal gas. Here condensation to one half has taken place.

## AQUA AMMONIÆ OR LIQUOR AMMONIÆ.

This most useful reagent is best prepared by causing the gas disengaged from the above mixture of sal-ammoniac and slacked lime by heat, a little water having been previously added to moisten the powder, to pass through cold water in an apparatus furnished with a safety-tube to prevent undue absorption, the gas being washed by means of a very little water placed in an intermediate bottle. The water, if kept cold, will absorb about 670 times its bulk of the gas, by which it is increased in bulk, acquires a Sp. G. of only 0·872, and becomes possessed of all the chemical properties of the gas in a very high degree. This is the aqua ammoniæ fortissima of the manufacturers, and for



medical use it requires to be diluted till it has the Sp. G. of 0·96. At 0·872, it contains 32·5 per cent. of dry gas; at 0·96, hardly 10 per cent. Hence, by adding 8 vol. of water to 3 vol. of the strongest ammonia, we reduce it to the ordinary medical strength, which is also sufficiently strong for the usual chemical purposes.

This solution is constantly employed by the chemist for neutralising acids, and precipitating insoluble bases. It has the very great advantage of not introducing any fixed matter, so that the re-agent may be totally expelled by a red-heat. In medicine it is much employed, internally, as a diffusible stimulant, and externally as a powerful rubefacient, and also along with oil as a counter irritant. If it can be procured in time, it is the best antidote to prussic acid.

With acids, ammonia forms salts, which are recognised by their yielding the pungent smell of ammonia when mixed with

caustic potash or slacked lime. They are either volatile in the fire, as carbonate, sulphate, &c. ; or they are decomposed, the ammonia being driven off and the acid remaining behind as in the case of phosphate of ammonia. For the constitution of the salts of ammonia, see below.

c. Ammonium.  $\text{NH}_4 = 18$ .

This compound, like amide, is not known in the separate state ; but we have reason to believe that it exists, and has the chemical relations of a metal : hence its name.

When a salt of ammonia is decomposed by galvanic electricity, the negative pole terminating in a drop of mercury, the mercury swells to many times its original bulk, becomes almost solid, but retains its metallic aspect. The same compound is much more easily and abundantly formed when an amalgam of mercury with potassium or sodium is placed in a warm solution at about  $100^\circ$ , of sal ammoniac. The mercury immediately begins to swell, and in a few minutes more than fills the whole liquid with a soft metallic mass, perhaps 100 times the volume of the amalgam of sodium employed. It is crystalline, and has been regarded as an amalgam of mercury and ammonium. When left in the liquid, it gives off ammonia and hydrogen, and the mercury resumes its original bulk. The remarkable circumstance is, that the amalgam contains so small a weight of ammonium (or of ammonia+hydrogen), although its properties are so different from those of the mercury. But, if we suppose an amalgam to be formed of 10 eq. of mercury and 1 eq. of ammonium, this would contain less than 2 per cent. of the latter. There is, therefore, nothing unreasonable or very improbable in the idea of a compound metal of ammonium,  $\text{NH}_4$ . Indeed, if we assume its existence, we are enabled to take a view of the constitution of the salts of ammonia, which makes them analogous to those of the other alkalies.

It was formerly the universal opinion that ammonia,  $\text{NH}_3$ , combined directly with oxygen acids, such as sulphuric acid,  $\text{SO}_3$ , as well as with hydrogen acids, such as hydrochloric acid,  $\text{HCl}$ . According to our present knowledge, the hydrochlorate of ammonia does really contain the elements  $\text{NH}_3 + \text{HCl}$ , although we may suppose them otherwise arranged : but it has been shown that dry or anhydrous sulphuric acid,  $\text{SO}_3$ , although it can be made to unite with ammonia, does not produce sulphate of ammonia ; but that the formation of this latter salt requires, besides the elements of ammonia and sulphuric acid, those of 1 eq. of water,  $\text{HO}$  ; and that the salts of ammonia, with the oxygen acids in general, contain, as an essential ingredient, this

1 eq. of water. It is not easy to see why ammonia should form neutral salts without the aid of water, when acted on by hydrogen acids, and should require water when combining with oxygen acids. But if we admit that ammonium exists, and is the true basic radical in all these salts, the whole becomes clear. In that case,  $\text{NH}_3 + \text{HO}$ , ammonia + 1 eq. of water, becomes  $\text{NH}_4\text{O}$ , or oxide of ammonium; sulphate of ammonia + water ( $\text{NH}_3, \text{HO} + \text{SO}_3$ ) becomes dry sulphate of oxide of ammonium,  $\text{NH}_4\text{O}, \text{SO}_3$ ; and hydrochlorate of ammonia,  $\text{NH}_3, \text{HCl}$ , becomes chloride of ammonium,  $\text{NH}_4\text{Cl}$ . It has been observed that the oxygen acid salts of ammonium + water are isomorphous with the dry salts of potash. Now, on the old view, we can trace no analogy between  $\text{NH}_3, \text{HO}, \text{SO}_3$ , and  $\text{KO}, \text{SO}_3$ ; but, if we admit the existence of the metal ammonium, and, still more, if we represent it by the symbol Am., the analogy becomes obvious. Thus we have the two series—

|                | Potassium.                     | Ammonium.                       | Do. at full length.                |
|----------------|--------------------------------|---------------------------------|------------------------------------|
| Metal . . .    | K . . .                        | Am . . .                        | $\text{NH}_4$                      |
| Oxide . . .    | KO . . .                       | AmO . . .                       | $\text{NH}_4\text{O}$              |
| Chloride . . . | KCl . . .                      | AmCl . . .                      | $\text{NH}_4\text{Cl}$             |
| Sulphate . . . | $\text{KO}, \text{SO}_3$ . . . | $\text{AmO}, \text{SO}_3$ . . . | $\text{NH}_4\text{O}, \text{SO}_3$ |

The only difference between the two series is, that we know Am. to be a compound, while K is, as yet, undecomposed. But, as formerly remarked, all our present elements may hereafter prove to be compounds; and even were this not so, we can easily conceive a compound metal playing the same part as a simple one.

We have to bear in mind that ammonium, if it exist, is resolved into ammonia,  $\text{NH}_3$  and hydrogen, whenever we attempt to isolate it: that ammonia in combining with a hydrated oxygen acid, such as  $\text{HO}, \text{SO}_3$ , takes the hydrogen of the water, forming ammonium  $\text{NH}_4$ ; which, with the oxygen of the water, produces oxide of ammonium, and that the oxide then unites with the acid: and, finally, that ammonia, in contact with a hydrogen acid, such as  $\text{HCl}$ , takes the hydrogen of the acid to form ammonium, which then unites with the acid radical chlorine. Indeed, this very simple view may be extended to the hydrated oxygen acids, if we view them as hydrogen acids. Hydrated sulphuric acid,  $\text{HO}, \text{SO}_3$ , may be viewed as a hydrogen acid,  $\text{H}, \text{SO}_4$ : and if ammonia act on this, we have either  $\text{NH}_3 + \text{HO}, \text{SO}_3 = \text{NH}_4\text{O}, \text{SO}_3$ : or  $\text{NH}_3 + \text{H}, \text{SO}_4 = \text{NH}_4, \text{SO}_4$ ; the latter being perfectly analogous to the formation of chloride of ammonium (sal-ammoniac),  $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$ .

The above is a sketch of the ammonium theory of Berzelius, which is beautifully consistent, if we once admit the existence of ammonium: rendered, as it is, so probable by the phenomena

of the amalgam, and by the isomorphism of the compounds of potash and those of ammonia + 1 eq. of water. This theory is pretty generally adopted by chemists.

Ammonia belongs strictly to organic chemistry, and on that account we shall return to it under that head. It is, indeed, the type of a very remarkable class of compounds, namely, the volatile organic bases, while oxide of ammonium appears to be the type of the fixed organic bases. Let us represent ammonia as follows :

$$\left. \begin{array}{c} \text{H} \\ \text{N H} \\ \text{H} \end{array} \right\} \text{ If one of the eqs. of hydrogen be replaced by a compound radical, such as methyle, } (C_2 H_3 = \text{Me}) \text{ or ethyle } (C_4 H_5 = \text{Ae}), \text{ we obtain the following compounds.}$$

$$\left. \begin{array}{c} \text{H} \\ \text{N H} \\ \text{Me} \end{array} \right\} \text{ and } \left. \begin{array}{c} \text{H} \\ \text{N H} \\ \text{Ae} \end{array} \right\} \text{ in which the type is unaltered ; so much so, that the first, methylamine, is a gas}$$

hardly to be distinguished from ammonia, and the second, ethylamine, a highly volatile liquid, closely analogous to ammonia in properties. And we can also obtain compounds in which the second eq. of hydrogen is also replaced, as

$$\left. \begin{array}{c} \text{H} \\ \text{N Me} \\ \text{Me} \end{array} \right\} \text{ and } \left. \begin{array}{c} \text{H} \\ \text{N Ae} \\ \text{Ae} \end{array} \right\} \text{ dimethylamine and diethylamine, as well as others in which all the hydrogen is replaced, as}$$

$$\left. \begin{array}{c} \text{Me} \\ \text{N Me} \\ \text{Me} \end{array} \right\} \text{ and } \left. \begin{array}{c} \text{Ae} \\ \text{N Ae} \\ \text{Ae} \end{array} \right\} \text{ trymethylamine and triethylamine and all of these are volatile bases. Many other radicals can produce similar basic compounds, all of which have the type of ammonia. They belong to organic chemistry, but are so important, and illustrate so well the high importance of ammonia, that I have thought it right briefly to notice them here, more especially as they admirably illustrate also the nature of chemical types and the law of substitution without change of type.}$$

But this is not all, for if we take hydrated oxide of ammonium,  $NH_4O$ ,  $HO$ , we find that compounds may be obtained in which all four eqs. of hydrogen are replaced by compound radicals, as  $N Me_4O$ ,  $HO$ , and  $NAe_4O$ ,  $HO$ , which may be called the hydrated oxides of tetramethylum and of tetrethylum. Now, as hydrated oxide of ammonium corresponds to hydrated oxide of potassium or caustic potash, so also do these new hydrated oxides ; and although that of ammonium cannot exist in the separate form, on account of the strong attraction of oxygen for the fourth eq. of hydrogen, (which splits the compound up into ammonia and water, thus,  $NH_4O$ ,  $HO = NH_3 + 2HO$ ), the hydrated oxides of tetramethylum and tetrethylum do exist in the free state, and are found to be just as analogous to caustic potash, as the

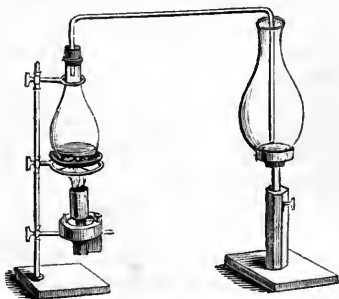
volatile bases are to ammonia. They are crystallisable, caustic, highly alkaline, and form soaps with oils; but besides this, they have a bitter taste and are decomposed by heat, yielding volatile bases, in which characters they agree with natural fixed organic bases, such as quinine and morphine, to which they approach so closely in composition. Indeed, Hofmann has actually produced a compound of this class, which, though not identical with quinine, has nearly the same composition. Many of the artificial fixed bases of this type are strikingly analogous to the natural bases. It is hardly necessary to point out how strongly these facts speak in favour of the theory of ammonium as a compound metal, analogous to potassium.

For details on this very important subject of the artificial organic bases, and their typical relation to ammonia and oxide of ammonium, the reader is referred to the Handbook of Organic Chemistry.

#### 4. CHLORINE. $\text{Cl} = 35.5$ .

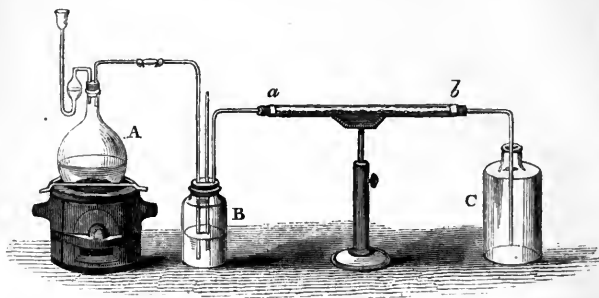
This element occurs in prodigious quantity in the well-known substance, sea or rock-salt, in which it is combined with sodium. It is also occasionally found in combination with lead, silver, and mercury. Chloride of potassium is a frequent ingredient of ashes, especially of the ashes of sea plants.

Chlorine is best prepared by the action of peroxide of manganese on hydrochloric acid. 1 part of finely-powdered peroxide is covered in a roomy flask with six parts of moderately strong hydrochloric acid (4 parts of concentrated acid and 2 of water); to the flask is fitted tightly a tube bent twice at right angles, the longer limb of which is conducted to the bottom of a dry, wide-mouthed bottle, furnished with a tight glass stopper. The chlorine, on the applica-



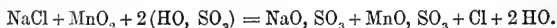
tion of a gentle warmth, escapes in the form of gas, and being much heavier than air, is very easily collected in dry vessels by displacement. As soon as the bottle is filled, which is easily seen from the yellow colour of the gas, it is withdrawn and replaced by another. If the gas is to be kept, the stopper must be tightly fitted into the bottle, and the juncture well greased. If the gas be required very pure and dry, it must be

passed, first through a bottle containing a little water and then through one with oil of vitriol. The first arrests any hydrochloric acid, the second removes all the water taken up in the first. Or a tube with chloride of calcium may be substituted for the second bottle, as in the figure.



The following equation shows the change :  $\text{MnO}_2 + 2 \text{HCl} = \text{MnCl} + 2 \text{HO} + \text{Cl}$ . Here one half of the chlorine is given off as gas, while the other remains behind as chloride of manganese.

The manufacturer uses another process, which is preferable where large quantities are required. 1 part of peroxide of manganese, 4 of sea-salt (chloride of sodium), 2 of oil of vitriol, with the addition of 2 of water, are heated together. Here the acid, acting on the salt, produces sulphate of soda and hydrochloric acid, which is decomposed as before by the peroxide of manganese, and the chloride of manganese thus formed is decomposed in the same way as the salt, yielding sulphate of protoxide of manganese and chlorine. Thus the whole chlorine of the salt is obtained, and the final result is expressed by the following equation :



Chlorine, at the usual temperature, is a gas which is liquefied by a pressure of about four atmospheres. It is transparent and of a strong yellowish-green colour (hence its name). Its Sp. G. is about 2.44, and 100 cubic inches weigh about 78 grains. Its smell is very disagreeable, pungent and suffocating ; when much diluted it recalls the smell of the air on the sea shore. If respired pure, it causes instant death ; and even when diluted with air, excites cough, pain, and a sense of stricture on the chest, often lasting for many hours, and only relieved by a very copious expectoration of thick mucus, but occasionally followed



by spitting of blood. The irritation thus caused may often give rise to permanent and serious disease of the lungs, and, therefore, care should be taken not to breathe the gas in working with it. It is not a little remarkable, however, that, if very much diluted, although still apt to excite cough, it is found to alleviate the symptoms of phthisis when inhaled, probably by promoting expectoration. The patients themselves soon learn to bear it stronger, and to long for the hour of inhaling it. It is also stated that the workers in manufactories of bleaching powder, and in bleaching and dye-works, where the air is always to some extent charged with chlorine, are less liable to phthisis than others, so that, up to a certain point, the system seems capable of becoming habituated to it with benefit.

Chlorine supports the combustion of many substances, such as a candle, which, however, burns with a dark red flame, and deposits a good deal of smoke. Many bodies take fire spontaneously in it, as phosphorus, antimony, oil of turpentine, &c. If a roll of paper be dipped in oil of turpentine, and then placed in a jar of chlorine, which, however, ought not to be dried, after a short interval a large red flame suddenly flashes out, while the jar is filled with black smoke and lined with a coating of carbonaceous matter. If 2 vols. of chlorine be mixed with 1 vol. of olefiant gas,  $C_4H_4$ , in a tall jar, and a light applied to the mouth of the jar, a red flame, followed by thick black smoke, slowly passes down the jar, lining it with carbon, while hydrochloric acid is largely disengaged. But if equal volumes of olefiant gas and chlorine be mixed, and placed over water, both gases disappear, and a volatile oily liquid, heavier than water, much resembling chloroform, is produced. The action in the former beautiful experiment is as follows:  $C_4H_4 + Cl_2 = 4HCl + C_4$ ; in the second it is  $C_4H_4 + Cl_2 = C_4H_3Cl, HCl$ . The latter formula is that of the oily liquid which is called the oil of olefiant gas (so named because it yields this oil), or the oil of the Dutch chemists, having been first observed by an association of chemists in Holland. Its proper name is hydrochlorate of chloride of acetylene. Acetylene is  $C_2H_2$ , and olefiant gas is its hyduret,  $C_4H_6$ ,  $H=C_4H_5$ . As tallow and wax consist chiefly of carbon and hydrogen, when they are burned in chlorine hydrochloric acid is formed, while much carbon is deposited. The above facts depend on the very feeble attraction of chlorine for carbon while its affinity for hydrogen is very strong. Like oxygen, chlorine may be made to burn in an atmosphere of hydrogen or of coal gas.

Chlorine gas dissolves in water: hence it cannot be preserved over that liquid. The solution is termed chlorine water. It

has the smell of the gas, and bleaches vegetable colours most powerfully, which perfectly dry chlorine does not. It also destroys foetid or noxious effluvia, and is very useful in checking the spread of contagious disease. With water, chlorine forms a crystalline hydrate,  $\text{Cl} + 10 \text{ aq.}$ , which, if heated in a bent tube, sealed at both ends, yields water and liquefied chlorine.

The affinities of chlorine for the metals are very powerful, frequently stronger than those of oxygen. It therefore decomposes many oxides, as well as bromides, iodides, sulphurets, &c., at ordinary temperatures, and almost all the rest at a red-heat. It acts so strongly on mercury that it cannot be collected over that metal. But its strongest affinity is to hydrogen, with which it forms hydrochloric acid. It is to this powerful affinity that the bleaching properties of chlorine are to be ascribed: it seizes on part of the hydrogen of the colouring matter, and thus decomposes it entirely. The same remark applies to the destruction of effluvia and miasmata.

The presence of free chlorine is detected by its smell and its power of bleaching solution of indigo. Nitrate of silver also causes with it a curdy white precipitate of chloride of silver, insoluble in acids. (See Hydrochloric Acid.)

The compounds of chlorine, which are not acids, are called chlorides. But though the metallic chlorides are not acids, in the usual sense, nor yet bases, it is to be observed that the perchlorides of certain metals, such as those of mercury, gold, platinum, palladium, iridium, and rhodium, are decidedly negative with respect to the protochlorides of the metals of the alkalis, including chloride of ammonium. It is probable that the negative character of the former is due to the large proportion of chlorine they contain, while the positive energy of the alkaline metals overpowers the negativity of the one atom of chlorine in their protochlorides. At all events these two classes of chlorides unite to form crystallisable and often very permanent salts. Tetrachloride of gold forms, for example, with chloride of sodium the salt  $\text{NaCl}, \text{AuCl}_3$ , or aurochloride of sodium, while the bichloride of platinum forms similar salts with the chlorides of potassium, sodium, and ammonium, three remarkable and useful salts, namely, the platinochloride of potassium,  $\text{KCl}, \text{PtCl}_2$ ; of sodium  $\text{NaCl}, \text{PtCl}_2$ , and of ammonium  $\text{NH}_4\text{Cl}, \text{PtCl}_2$ . The bichloride of mercury, and the perchloride of the other metals above named, form analogous compounds, in which the perchlorides play the part of acid or negative constituent, the protochlorides that of base or positive constituent.

As chloride of ammonium, or hydrochlorate of ammonia,

$\text{NH}_4\text{Cl}$  or  $\text{NH}_3$ ,  $\text{HCl}$ , combines in this way with bichloride of platinum, so also do the hydrochlorates of all the volatile organic bases of the type of ammonia, such as methylamine. These hydrochlorates may of course also be viewed as chlorides; thus that of methylamine  $\text{C}_2\text{H}_5\text{N}$ ,  $\text{HCl}$ , may be considered as chloride of methylium,  $\text{C}_2\text{H}_5\text{N}$ ,  $\text{Cl}$ , &c., &c. In like manner as chloride of potassium combines with bichloride of platinum, so also the chlorides of the fixed bases of the type of potash do the same. Thus chloride of tetramethylium forms with bichloride of platinum a salt strikingly analogous to the platino-chloride of potassium, the formula of which, at full length, is  $\text{C}_8\text{H}_{12}\text{NCl}$ ,  $\text{PtCl}_2$ ; or abbreviated  $\text{NMe}_4\text{Cl}$ ,  $\text{PtCl}_2$ , in which latter shape we see its analogy, not only with the potassium salt  $\text{KCl}$ ,  $\text{PtCl}_2$ , but with the ammonium one  $\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_2$ . In fact, it is a universal character of organic bases, probably because they all belong either to the type of ammonia or to that of potash, that they form such salts with bichloride of platinum. And as the salts thus formed are, in most cases, easily purified, and admit of exact analysis, no class of compounds has contributed more to the advancement of knowledge in organic chemistry. For this reason I have explained fully the value of the perchlorides of the noble metals in this place.

#### SOLUTION OF CHLORINE.

This solution is prepared by simply passing a slow current of chlorine gas through water (previously boiled and allowed to cool), placed in inverted retorts nearly full. As soon as water begins to escape at the neck of one retort, the tube is transferred to another, and so on alternately till the water refuses to absorb any more. The solution, which has the colour, smell, and bleaching properties of the gas, must be kept in small bottles, quite filled, and closely fitted with glass-stoppers. A drachm or more of this, added to about four or six ounces of water at  $100^\circ$ , forms a mixture through which air may be drawn into the lungs when we wish diluted chlorine to be inhaled. The solution is decomposed by light, and ought, therefore, to be kept in the dark. Under the influence of light, chlorine, in virtue of its strong attraction for hydrogen, decomposes the water of the solution, forming hydrochloric acid, while oxygen is liberated.

Chlorine combines both with oxygen and hydrogen, but as the compound of chlorine with hydrogen is the most important, we shall here deviate slightly from the natural order and treat of it first.

## CHLORINE AND HYDROGEN.

Hydrochloric Acid.  $\text{HCl} = 36.5$ .

**SYN. *Muriatic Acid***—Is formed when equal volumes of chlorine and hydrogen are mixed and exposed to sun-light, flame, or the electric spark, all of which cause the gases to combine with explosion. Is best prepared by the action of sulphuric acid on sea-salt, when the gas is disengaged even without the aid of heat. As water instantly absorbs it, it must be collected over mercury, or by displacement, as it is somewhat heavier than air.

The following equation shows the formation of the acid:—  
 $\text{NaCl} + (\text{HO}, \text{SO}_3) = \text{HCl} + (\text{NaO}, \text{SO}_3)$ : or,  $\text{NaCl} + \text{H}, \text{SO}_4 = \text{HCl} + \text{Na}, \text{SO}_4$ .

Hydrochloric acid is a gas, transparent and colourless, fuming strongly with moist air, of a pungent acid, suffocating smell, and a strong sour taste. Its Sp. G. is the mean between those of chlorine and hydrogen, or 1.247, it being formed of equal volumes of these gases without condensation. By a pressure of 40 atmospheres it may be condensed into a liquid of Sp. G. 1.27. It is absorbed in large proportion by water, forming the common or liquid hydrochloric acid, which is merely a solution of the gas in water. A fragment of ice introduced into the gas over mercury instantly liquefies, the gas being as quickly absorbed. This solution reddens, but does not bleach, vegetable blue colours; and neutralises the alkalies, yielding neutral salts, which are found to be chlorides.

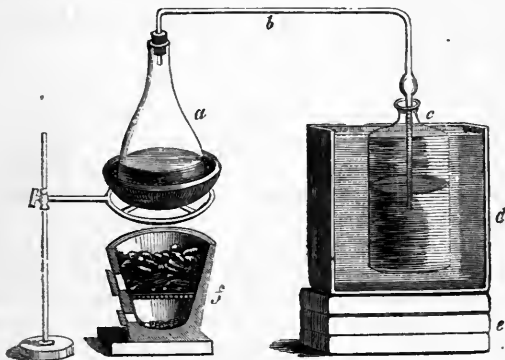
When it acts on soda,  $\text{NaO}$ , for example, we obtain neutral crystals by evaporation, but these are found to be sea-salt,  $\text{NaCl}$ , and contain neither oxygen nor hydrogen, so that these latter elements must have united to form water; thus  $\text{NaO} + \text{HCl} = \text{NaCl} + \text{HO}$ . The result is, in regard to neutrality, the same as if the acid and alkali had directly combined together and neutralised each other: for the chloride of sodium ( $\text{NaCl}$ ) and water are both neutral. The general formula for the action of this and similar hydrogen acids on metallic oxides is as follows:  $\text{HR} + \text{MO} = \text{MR} + \text{HO}$ . Here,  $\text{R}$  stands for chlorine or any other acid radical, and  $\text{M}$  for any metal. If the oxide be a sesquioxide, the formula will be  $3\text{HR} + \text{M}_2\text{O}_3 = \text{M}_2\text{R}_3 + 3\text{HO}$ . Here, 3 eq. of hydrogen acid and 1 eq. of sesquioxide yield 1 eq. of sesquichloride (bromide, iodide, &c.) and 3 eq. of water; but the principle is the same. In some cases, however, hydrochloric acid appears to combine with oxides; as with alumina or oxide of chromium.

It will be easily seen, from what has just been said, that the action of hydrochloric acid on oxides affords a ready and convenient means of obtaining the corresponding chlorides. This method is very often employed.

## HYDROCHLORIC ACID AND WATER.

## LIQUID, OR AQUEOUS HYDROCHLORIC ACID.

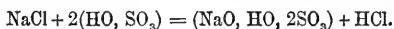
SYN. *Liquid Muriatic Acid: Spirit of Salt*.—This most indispensable re-agent is best prepared, as I have shown, by the following easy process, which moreover yields it perfectly pure : 6 parts, by weight, of pure salt are introduced into a flask or matrass, and covered with ten parts by weight of oil of vitriol,



and 4 parts of water, the latter having been previously mixed, and the mixture allowed to cool : or we may take 8·5 parts, by measure of sulphuric acid, Sp. G. 1·65. No action takes place in the cold, so that we may adapt securely a bent tube to convey the gas to the flask. This tube is twice bent at right angles, and has a bulb blown on the longer descending limb. In a bottle, surrounded with ice-cold water, is placed a quantity of distilled water equal in weight to the salt, and the bent tube is made to dip about  $\frac{1}{8}$  inch into this water. A gentle heat is now applied to the flask, which rests in a sand-pot, and continued as long as any hydrochloric acid comes over. In about three hours the process is finished, and we find the distilled water increased in volume nearly two-thirds, and converted into hydrochloric acid, quite pure and colourless, of Sp. G. 1·14 to 1·15. If we wish it as strong as possible, or of Sp. G. 1·21, we have only to employ, in a second operation, a part of the acid above described in the

place of the distilled water, during the first half of the operation, when it will speedily become saturated. No safety-tube is required : it is only necessary to lower the bottle a little, occasionally, so that the tube shall never dip far into the liquid : and even should absorption take place too rapidly, and the water rise in the tube, the bulb will receive it, the end of the tube will be exposed, and air entering will prevent the regurgitation of the water into the flask. This simple tube, therefore, forms a self-acting valve, and renders a safety-tube unnecessary. The absorbing liquid must be kept as cold as possible, by frequently changing the surrounding water, which becomes warm owing to the heat developed in the absorption. If ice can be had, a little added to the cooling-vessel, from time to time, keeps the temperature sufficiently low.

✓ In the above operation, the proportions of acid and salt are according to the formula



Here, 2 eq. of acid are employed for one of salt ; for two reasons. First, a much lower heat is required ; and 2ndly, the resulting salt, bisulphate of soda, is quite easily got out, without risking the flask, which is not the case when 1 eq. of acid is used, and neutral sulphate is left. The acid is diluted to Sp. G. 1·65, or even 1·60 for the same reasons. The addition of the water facilitates the operation, and renders the resulting mass more soluble and manageable. It is to be observed that notwithstanding this addition of water  $\frac{2}{3}$  of the hydrochloric acid gas comes off quite dry, and it is only towards the end of the operation that, the heat being increased, water and acid come off together. This is easily known by the tube becoming hot from the condensation of the steam. From first to last, not a trace of sulphuric acid passes over, even into the tube ; and thus by using tolerably pure materials, we obtain colourless and pure hydrochloric acid as easily and cheaply as if we were making the very impure acid of commerce. By the above process, the purest and strongest hydrochloric acid might be sold for not more than 3*d.* per lb., probably for much less.

Pure aqueous hydrochloric acid has, when concentrated, a Sp. G. of 1·21, and fumes strongly when exposed to the air, the gas constantly escaping and uniting with the vapour which it meets. The acid even fumes when no denser than 1·13, and acid of from 1·14 to 1·16 is most convenient for common use, as there is not so much gas lost from it as from the strongest. It ought to be quite colourless ; if yellow, it contains perchloride of iron or free chlorine, probably both. The liquid is very acid and

corrosive. When a rod dipped in aqua ammoniæ is brought near, very thick white fumes of sal-ammoniac are formed. If heated, gas is expelled, the boiling point, which is at first very low, gradually rising, till the Sp. G. falls to 1·100, when the boiling point is rather higher than that of water ; and at this strength the acid distils over unchanged. A weaker acid, if boiled, loses water, and becomes stronger, while a stronger, as we have seen, loses gas and becomes weaker. We can, therefore, purify the common acid by diluting it to Sp. G. 1·100, and distilling it, rejecting the first and last portions. The intermediate portion is pure, but cannot in this way be obtained concentrated.

The presence of hydrochloric acid is detected by nitrate of silver, which forms, even in very diluted solutions, a white curdy precipitate of chloride of silver, insoluble in acids. It is to be borne in mind, however, that the presence of free chlorine and soluble chlorides give rise to the same compound : we must, therefore, ascertain their absence, and the presence of an acid, before we can rely on this test.

The muriatic acid of commerce is very impure. It contains fixed impurities, detected by evaporation to dryness ; sulphuric acid, detected by adding to the liquid, first distilled water, and then a salt of barium ; chloride of iron, detected by ferrocyanide of potassium ; free chlorine, recognised by its power of dissolving gold ; and sulphurous acid, easily known by its smell. It often also contains tin and arsenic, which may be discovered by the proper tests of those metals. As no re-agent is so much employed by the chemist, and none so necessary to have perfectly pure, the chemist ought never, in careful experiments, to use the common acid ; and it is on this account that I have so minutely described the method which I have given for obtaining it pure, and which is now generally adopted in the Continental laboratories.

Hydrochloric acid is much used in chemical investigations, chiefly for dissolving inorganic bases, with most of which it forms soluble chlorides : the exceptions are oxide of silver and protoxide of mercury, the chlorides corresponding to which are insoluble ; and protoxide of lead, which yields a sparingly soluble chloride. In all inorganic researches, and, above all, in the analysis of minerals, soils, &c., it is absolutely indispensable.

Hydrochloric acid may be viewed as the type of all acids, including the so-called hydrated oxygen acids. We shall have occasion to return to this subject when treating of the acids of sulphur, and also in the general remarks on salts.

## NITRO-MURIATIC, OR NITRO-HYDROCHLORIC ACID.

SYN. *Aqua Regia*. This mixture, which is usually made with one vol. of nitric to two or three of hydrochloric acid, has long been known, and used for dissolving gold and platinum, which do not dissolve in either of the acids, when separate. The nature of the action between the acids has been variously interpreted, but the researches of Gay-Lussac appear to have finally cleared it up. When the mixture is gently heated, free chlorine, accompanied by red vapours, escapes. The red vapours are those of a new compound, which may be condensed in a cold receiver, and which has been called chloronitric acid, the formula of which is  $\text{NO}_2\text{Cl}_2$ . It is nitrous acid, in which 2 eq. of oxygen are replaced by 2 eq. of chlorine, and ought perhaps to be called chloronitrous acid; but that name has been given to another compound. The action is as follows:  $\text{NO}_5, \text{HO} + 3\text{HCl} = \text{NO}_2\text{Cl}_2 + 4\text{HO} + \text{Cl}$ . The chloronitric acid is decomposed by water, as follows:  $\text{NO}_2\text{Cl}_2 + 2\text{HO} = 2\text{HCl} + \text{NO}_4$ .

In the latter stages of the action of nitric on hydrochloric acid, another new compound is formed, which has been called chloronitrous acid, the formula of which is,  $\text{NO}_2\text{Cl}$ , and which is hyponitrous acid, with 1 eq. of chlorine replacing one of oxygen. The theory of its formation is not certainly known; but it may be that the same proportions, at a higher temperature, are decomposed as follows:  $\text{NO}_5 + 3\text{HCl} = 3\text{HO} + \text{NO}_2\text{Cl}$ . Chloronitrous acid, which seems to be gaseous at ordinary temperatures, is also formed when deutoxide of nitrogen is mixed with half its volume of chlorine. It has a deep orange colour.

Although both chloronitric and chloronitrous acids are present in aqua regia, they do not possess the power of dissolving gold or platinum. These metals are dissolved by the chlorine, which comes in contact with them when it is in the nascent state. Hence it is the perchlorides of these metals which are formed, and by evaporating to dryness with excess of hydrochloric acid, the nitric acid is totally decomposed, and the chlorides obtained in a state of purity.

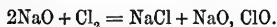
## CHLORINE AND OXYGEN.

The affinity of chlorine for oxygen is very feeble, and these elements cannot be made to combine directly. By indirect means, however, they may be made to unite, and four compounds are known, all of which are acids.



a. Hypochlorous Acid.  $\text{ClO} = 43.5$ .

SYN. *Acide hypochloreux. Unterchlorige Säure.* — When chlorine gas is passed through a cold diluted solution of an alkali, compounds are formed, which are known as bleaching compounds, and have been considered to consist of chlorine and metallic oxides, such as the so-called chlorides of lime and soda. They are, however, in reality mixtures of chloride of the metal with hypochlorite of the oxide. Thus 2 eq. of soda and 2 eq. of chlorine, instead of combining together, act on each other as follows :—



The true bleaching compound of soda contains, therefore, 1 eq. of chloride of sodium + 1 eq. of hypochlorite of soda.

To obtain hypochlorous acid in the free state, red oxide of mercury and water are agitated with chlorine : when there are formed a compound of perchloride and peroxide of mercury, which is insoluble, and hypochlorous acid which dissolves in the water.



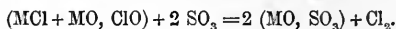
By rectification, a stronger solution may be obtained ; and if this be placed in a retort with an excess of dry nitrate of lime, this salt seizes on the water, and the hypochlorous acid gas separates and may be collected over a saturated solution of nitrate of lime.

It is a gas of a strong yellow colour, and a peculiar penetrating smell. It is very easily decomposed into two vol. of chlorine, and one vol. of oxygen, exploding by the mere contact of many combustible substances, or by a gentle heat. Experiments with it require the greatest caution.

Water absorbs about 100 times its volume of this gas, and acquires a pale yellow colour, and the astringent, not acid, taste and peculiar smell of the gas. It bleaches powerfully, and is easily decomposed by all substances which have a strong affinity for chlorine or for oxygen. It is therefore a powerful oxidising agent. According to Gay-Lussac its bleaching power is equal to twice that of the chlorine it contains.

With the stronger bases it unites, forming salts which are called hypochlorites, the general formula of which is  $\text{MO}, \text{ClO}$ . With acids these salts yield hypochlorous acid, not chlorine ; and they are thus distinguished from the true bleaching salts, which, when acted on by acids, yield pure chlorine. The bleaching salts have the general formula  $\text{MCl} + \text{MO}, \text{ClO}$  ; that is,

as already stated, they are mixtures or compounds of chlorides and hypochlorites. Of these salts that of lime, or bleaching powder, is the most important. It is made by exposing slaked lime, that is, dry hydrate of lime, to chlorine gas, stirring the powder frequently to promote absorption. But the whole of the lime is never thus converted into the bleaching compound. This can only be effected by suspending slaked lime in water, and passing chlorine gas through it till all is dissolved. The action of sulphuric acid on bleaching compounds is as follows:—



Here all the chlorine, both that of the chloride, and that of the hypochlorite, is given off in the free state. Hence, as chlorine is the real bleaching agent, the great bleaching power of the chlorides of lime and soda, as they are called, becomes intelligible. The action of dilute sulphuric acid on bleaching powder (chloride of lime, or  $CaCl + CaO, ClO$ ) furnishes a very easy and economical method of disengaging rapidly a large quantity of chlorine gas, as in fumigating a large room or house; no heat is required; we have only from time to time to add a table-spoonful of bleaching-powder to a basin of diluted acid.

When boiled, the hypochlorites as well as the bleaching compounds, which consist of hypochlorite + chloride, are resolved into chlorides and chlorates. Thus 3 eq. of hypochlorite of potash  $3 (KO, ClO)$  yield 1 eq. of chlorate of potash,  $KO, ClO_3$ , and 2 eq. of chloride of potassium,  $2KCl$ . Of course, if, as in the bleaching compound of potash, 3 eq. of hypochlorite were mixed with 3 eq. of chloride, the result would be 1 eq. of chlorate, and 5 eq. of chloride.

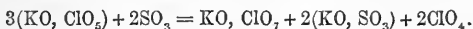
As the value of bleaching powder depends entirely on the amount of chlorine liberated from it by acid, and as this amount is variable, because from the mode of manufacture the powder is never a pure bleaching compound, but contains variable and often large quantities of uncombined hydrate of lime, it is desirable to have some method of ascertaining the percentage of chlorine in any specimen of the powder. One method is to mix a weighed portion with water, and add to it a solution of indigo in sulphuric acid (of a known strength, so that a certain volume of it is bleached by a certain weight of chlorine), as long as a bleaching action is exerted. Another, and perhaps a more accurate one, is to ascertain how much protosulphate of iron a given weight of bleaching powder will peroxidise, or taking a fixed quantity of the protosulphate, such as is peroxidised by 10, 20, 50, or 100 grains of chlorine, to ascertain how much bleaching powder is required to peroxidise it. The progress of the

oxidation is ascertained by means of the red prussiate of potash, which forms prussian blue as long as any protoxide of iron is left, but has no effect on the peroxide.

b. Chlorous Acid.  $\text{ClO}_2 = 67.5$ .

SYN. *Peroxide of Chlorine. Unterchlorsäure. Acide Hypochlorique.*—This acid is obtained by mixing oil of vitriol very gradually and cautiously with chlorate of potash, and applying to the yellow pasty mass thus formed, in a retort placed in a bath of proof spirit, a very gentle heat. Chlorous acid is given off as a deep yellow gas, which is even more easily decomposed, and more explosive than the preceding acid. Hence very great caution, and the use of a glass mask, are necessary in experimenting with it. It may be collected over mercury. Its smell is peculiar, almost aromatic. It is absorbed by water, which acquires its odour, and its bleaching properties.

The following equation explains its formation :—



That is 3 eq. of chlorate of potash, and 2 eq. of sulphuric acid, yield 1 eq. of perchlorate of potash, and 2 eq. of sulphate of potash, and 2 eq. of chlorous acid.

The compounds of chlorous acid with bases are not much known. In contact with alkalis, chlorous acid appears to be resolved into chloric and hypochlorous acids. Thus,  $4\text{ClO}_2 = 3\text{ClO}_3 + \text{ClO}$ .

c. Chloric Acid.  $\text{ClO}_3 = 75.5$ .

SYN. *Hyperoxymuriatic Acid.*—This acid is formed, as we have seen, in combination with a base, under different circumstances ; as, when the solution of a hypochlorite is boiled ; when chlorine is passed through a hot and strong solution of an alkali ; and when chlorous acid is brought into contact with bases. It is evident that in the second case a hypochlorite is formed, but is by the heat as rapidly destroyed, yielding a chlorate ; and if we suppose 6 eq. of potash to be acted on by 6 eq. of chlorine, we may suppose the first stage to be represented as follows :—



And in the second stage, the 3KCl remaining unchanged, we have

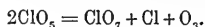


Or, omitting the first stage, as temporary only in the heat, we have



To obtain chloric acid, chlorate of baryta is dissolved in water, and sulphuric acid is added, so as exactly to precipitate all the baryta as sulphate. The clear solution is concentrated by spontaneous evaporation.

When very strong, it forms a yellowish oily-looking liquid, very sour to the taste. A piece of paper dipped in it soon takes fire, from the ease with which the acid yields its oxygen. It is resolved by distillation into hyperchloric acid, oxygen, and chlorine.



The salts of this acid, which are called chlorates, are quite permanent, but readily explode with combustible matter at a red-heat; or, in some cases, by friction and percussion alone, or by contact of oil of vitriol. Thus phosphorus and charcoal explode most violently in contact with chlorate of potash—the latter by friction, the former by percussion; and a kind of instantaneous light, formerly much used, consisted of a mixture of chlorate of potash, sugar, and a little gum, to make it adhere, placed on the end of a match, and dipped into oil of vitriol, when it took fire. The lucifers now used are also made with the same salt, and take fire by friction.

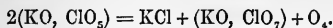
d. Perchloric Acid.  $\text{ClO}_4 = 91.5$ .

SYN. *Hyperchloric Acid*.—This acid may be obtained either by the distillation of chloric acid (see above), or by the distillation of hyperchlorate of potash with an equal weight of oil of vitriol, previously mixed with half as much water. It is purified from sulphuric acid by means of baryta, from chlorine by oxide of silver; and is then concentrated by slow evaporation.

It resembles the preceding acid, and when very concentrated, has a Sp. G. of 1.65. It reddens litmus without bleaching it, boils at  $412^\circ$ , and may be distilled without change. It is very permanent, and has strong affinities. Its best known salt is the perchlorate of potash, which is so sparingly soluble, that the acid may be used as a test for potash in all liquids not too diluted. As the perchlorate of soda is very soluble, the use of this acid enables us to distinguish, and to separate soda from potash.

The perchlorate of potash is easily formed by melting chlorate of potash, and heating it till the mass becomes thick and pasty, which takes place when  $\frac{1}{3}$  of the oxygen is expelled. The residue is a mixture of chloride of potassium and perchlorate of potash, and the latter is easily purified by dissolving the

whole in hot water, and allowing it to crystallise on cooling. The action of heat on chlorate of potash is thus expressed :—



It must here be observed, that our knowledge of the compounds of chlorine and oxygen is far from being complete or satisfactory, and that Gay-Lussac and Millon, since the discovery by Balard of hypochlorous acid, have devoted attention to the subject. Millon, indeed, has published an elaborate memoir, in which he describes, under the name of chlorous acid, a compound  $\text{ClO}_3$ , while he gives to the chlorous acid above described the name of hypochloric acid. The compound discovered by Davy, by acting on chlorate of potash with hydrochloric acid, and by him called euchlorine, by others protoxide of chlorine, and supposed by some to be a mixture of chlorine and chlorous acid ( $\text{ClO}_4$ ), by others to be identical with chlorous acid, is, according to Millon, composed of  $\text{Cl}_3\text{O}_{13} = 2\text{ClO}_3 + \text{ClO}_7$ . He calls it chlorochloric acid, and views it as composed of chlorous acid ( $\text{ClO}_3$ ) and perchloric acid. In like manner, Millon has described another acid, obtained by the action of light on his chlorous acid in contact with cold water, and which he calls chloroperchloric acid. It is composed of  $\text{Cl}_3\text{O}_{17} = \text{ClO}_3 + 2\text{ClO}_7$ , and differs from the last in the proportion of chlorous and perchloric acids it contains.

Almost all of the compounds have properties so similar that they are with difficulty distinguished from each other. Thus there are not less than 5 compounds, according to Millon, namely  $\text{ClO}$ ,  $\text{ClO}_3$ ,  $\text{ClO}_4$ ,  $\text{Cl}_3\text{O}_{13}$ , and  $\text{Cl}_3\text{O}_{17}$ , which are volatile liquids, yielding deep yellow highly explosive vapours. He distinguishes  $\text{ClO}$  and  $\text{ClO}_3$  from the others, as forming permanent salts with bases; the other three yield, with bases, a mixture of chlorate with chlorite (the acid in the latter being Millon's chlorous acid,  $\text{ClO}_3$ ), and the proportion of these salts is different in each case.

We have not space to enter more minutely into this very difficult but interesting subject. The researches of Millon are hardly completed, and require confirmation. In the meantime, the following table contains the compounds admitted by him, with his view of their true constitution :—

|                       |       |                            |  |
|-----------------------|-------|----------------------------|--|
| Hypochlorous acid     | . . . | $\text{ClO}$               |  |
| Chlorous acid         | . . . | $\text{ClO}_3$             |  |
| Hypochloric acid      | . . . | $\text{ClO}_4$             | $= \text{Cl}_4\text{O}_{16} = 3 \text{ClO}_3 + \text{ClO}_7$ |
| Chloric acid          | . . . | $\text{ClO}_5$             | $= \text{Cl}_2\text{O}_{10} = \text{ClO}_3 + \text{ClO}_7$   |
| Chlorochloric acid    | . . . | $\text{Cl}_3\text{O}_{13}$ | $= 2\text{ClO}_3 + \text{ClO}_7$                             |
| Chloroperchloric acid | . . . | $\text{Cl}_3\text{O}_{17}$ | $= \text{ClO}_3 + 2 \text{ClO}_7$                            |
| Perchloric acid       | . . . | $\text{ClO}_7$             | $=$  |

It will easily be seen that Millon admits, as independent compounds, only  $\text{ClO}$ ,  $\text{ClO}_3$ , and  $\text{ClO}_7$ ; and that he considers all the others as compounds of  $\text{ClO}_3$  with  $\text{ClO}_7$ , in various proportions. This readily explains the formation of perchlorate of potash from chlorate: for on this view, chlorate of potash is  $\text{KO}$ ,  $\text{ClO}_7 + \text{KO}$ ,  $\text{ClO}_3$ ; and when heated, it is the latter (the chlorite) alone which is at first decomposed into chloride of potassium and oxygen. On this view also, we see why all the three compounds,  $\text{ClO}_4$ ,  $\text{Cl}_3\text{O}_{13}$ , and  $\text{Cl}_3\text{O}_{17}$ , have properties so similar, and why they all yield, with potash, mixtures of chlorate and chlorite. For the details of the preparation and properties of these compounds, I must refer to the memoir of Millon, which is in the *Annales de Chimie et de Physique*, 1843, also in Liebig's *Annalen*, xlv. 281.

#### CHLORINE AND NITROGEN.

Perchloride of Nitrogen.  $\text{NCl}_4 = 156$ .

**SYN.** *Quadrichloride of Nitrogen*.—This compound is obtained by allowing chlorine gas to come in contact with a solution of sal-ammoniac at  $90^\circ$  or  $100^\circ$ . The gas is slowly absorbed, and an oily liquid appears in large drops on the surface of the solution. By agitating the vessel, these fall down, being heavier than the solution, and should be received in a thick cup of lead, kept very clean.

The perchloride of nitrogen is a yellowish oily liquid, distinguished for its tendency to explode by the mere contact of combustible matter, such as fat, oil, essential oils, phosphorus, &c. &c. The explosion is so violent, that even one drop of the liquid infallibly shatters to pieces any basin or bottle in which it explodes; and as it explodes often without any obvious cause, possibly from the contact of some minute portion of greasy matter, it is most dangerous to experiment on. A strong mask should be worn, and all the vessels employed should be scrupulously clean if it is necessary to make such experiments: it is better, however, not to attempt them. Both Dulong, the discoverer, and Davy, suffered very severely from their researches on it. Each lost an eye, and the former lost several fingers also. For the sake of illustration, a drop or two may be exploded in the lead cup above mentioned, by simply touching them with a rod dipped in oil. The results of the explosion are chlorine and nitrogeng ases. It is generally supposed that the formula of the compound is  $\text{NCl}_4$ , and its formation may be thus explained,  $\text{NH}_3, \text{HCl} + \text{Cl}_7 = 4\text{HCl} + \text{NCl}_4$ . But the composition of this substance cannot be considered as thoroughly ascertained,

and according to some it contains hydrogen in addition to chlorine and nitrogen.

5. BROMINE. Br.=80.

This element is found in minute proportion in sea-water, which generally contains about 1 grain per gallon ; in somewhat larger quantity in the water of the Dead Sea ; in the bittern or mother liquor of sea-water, out of which the sea-salt has been crystallised, and in the mother liquid of many salt springs, from which, in like manner, the sea-salt has been separated. The mother liquor of the salt springs at Kreuznach is particularly rich in bromine. In all these cases, the bromine occurs as bromide of potassium, sodium, or magnesium.

To obtain it, the liquor, concentrated as much as possible, is exposed to a current of chlorine gas, which is continued as long as the liquid becomes darker in colour from the bromine which is set free. The orange liquid thus obtained is to be agitated with ether, which rises to the surface, carrying with it all the bromine dissolved, which gives to the ether a hyacinth-red colour. The solution of bromine in ether is then acted on by a slight excess of potash, which produces a mixture of bromate of potash and bromide of potassium :  $6\text{KO} + 6\text{Br} = 5\text{KBr} + (\text{KO}, \text{BrO}_3)$ . The whole is dried and ignited, when all the oxygen of the bromate is expelled, and only KBr is left. This bromide is mixed with rather more than half its weight of peroxide of manganese, and then distilled along with its own weight of oil of vitriol (previously mixed with half its weight of water) ; the red vapours of bromine are given off and condensed in a tube or receiver very well cooled. By rectification with a little chloride of calcium, the bromine is obtained dry and pure. The following is the action of the sulphuric acid on the bromide of potassium and peroxide of manganese :  $\text{KBr} + \text{MnO}_2 + 2\text{SO}_3 = \text{KO},\text{SO}_3 + \text{MnO},\text{SO}_3 + \text{Br}$ .

Bromine is, at ordinary temperatures, a deep brownish-red liquid, boiling at  $113^\circ$  ; its Sp. G. is 2.97. Its vapour resembles that of nitrous acid, but has a very peculiar disagreeable pungent smell. It is poisonous, and acts so strongly on the lining membrane of the nose, that the mere smelling to a bottle of bromine is often followed by a painful sensation in the nostrils, attended with a copious flow of tears, lasting for hours, or even for days.

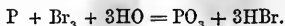
In all its relations, bromine is closely analogous to chlorine. It supports the combustion of phosphorus, and of many metals, like chlorine, and it bleaches organic colours. With hydrogen it forms hydrobromic acid, exactly analogous to hydrochloric

acid ; with oxygen it forms as yet only one acid,  $\text{BrO}_3$ , analogous to chloric acid. The analogy is equally striking when we compare the metallic bromides with the corresponding chlorides. Having so minutely described the relations of chlorine, this analogy will enable us to describe those of bromine very briefly. The affinities of bromine are less powerful than those of chlorine, so that the latter element disengages bromine from its compounds.

#### BROMINE AND HYDROGEN.

Hydrobromic Acid.  $\text{HBr} = 81$ .

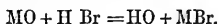
To obtain this acid, phosphorus, bromine, and a little water are placed in contact, and the gas which is disengaged is collected over mercury. The change is the following :—



Here, along with hydrobromic acid, phosphorous acid is produced. The acid may also be obtained by acting on bromide of potassium, with a strong solution of phosphoric acid.

Hydrobromic acid is a gas, transparent and colourless, fuming strongly when mixed with the air. Its Sp. G. is 2.73. It is, in smell, taste, absorbability by water, and indeed all its properties, hardly distinguishable from hydrochloric acid ; but chlorine decomposes it, setting free its bromine. The strongest solution of the acid is a fuming liquid of Sp. G. 1.29.

With metallic oxides it forms water and bromides, exactly as was explained under hydrochloric acid.



The bromides of lead, mercury, and silver, like the corresponding chlorides, are insoluble : the other bromides are soluble.

#### BROMINE AND OXYGEN.

Bromic Acid.  $\text{BrO}_3 = 120$ .

It has been already mentioned that bromic acid is formed in combination with potash, when bromine is acted on by that alkali. The bromate of potash is quite analogous to the chlorate ; and bromic acid may be obtained in the same way as chloric acid, by the action of fluosilicic acid on the bromate of potash, or of sulphuric acid on bromate of baryta. Its properties are quite analogous to those of chloric acid.

There is some reason to think that bromine forms bleaching compounds, which, like those of chlorine, contain peculiar acids,



bromous or hypobromous acids ; and it is also probable that there exists a perbromic acid, analogous to perchloric acid. Our knowledge of these compounds, however, is very limited.

With nitrogen, bromine is said to form an explosive oily liquid, analogous to chloride of nitrogen. But the composition of this substance is not ascertained. With chlorine bromine forms a reddish-yellow, volatile, pungent liquid, which is said to be  $\text{BrCl}_5$ , a perchloride of bromine. When this substance is acted on by potash, it yields chloride of potassium and bromate of potash.



#### 6. IODINE. 1 = 127.1.

Iodine occurs in maritime vegetables, and is found rather more abundantly in their ashes, as iodide of potassium, sodium, or magnesium. It is, of course, present in sea-water, but in so small a proportion as not to be easily detected. Iodide of silver has been found in Mexico, and some of the Silesian ores of zinc contain iodine.

It is best obtained from kelp, the ashes of various species of fucus, or other algæ. The kelp is lixiviated with water and the solution evaporated as long as it deposits crystals. The mother liquor is precipitated by a mixture of 1 part of sulphate of copper and  $2\frac{1}{4}$  parts of sulphate of iron, and the precipitate, which is subiodide of copper,  $\text{Cu}_2\text{I}$ , if heated with peroxide of manganese alone, or with the addition of sulphuric acid, yields the iodine as a purple vapour, which condenses in black crystalline scales on the cold part of the apparatus. It is purified by a second sublimation. Or the uncrystallisable mother liquid of kelp is mixed with an excess of sulphuric acid, which causes the disengagement of much sulphuretted hydrogen and sulphurous acid, while sulphur is deposited, and on cooling many crystals are formed, chiefly sulphate of soda. The acid liquid is placed in a leaden still, and warmed to about  $140^\circ$ . Peroxide of manganese is now added, and the heat gradually raised to  $212^\circ$ . The iodine is set free by an action similar to that explained under chlorine and bromine, and is collected in a succession of glass receivers connected together. It is accompanied by some water, the presence of which enables it to be sublimed at so low a temperature. This latter process is followed at Glasgow, where much iodine is manufactured.

At ordinary temperatures iodine is solid, of a bluish-black colour, and metallic lustre, like plumbago. It is often seen in acute rhomboidal plates ; it is very brittle, and its Sp. G. is

4·948. It melts at  $220^{\circ}$ , and is converted, when dry, into purple vapour at  $347^{\circ}$ . Along with the vapour of water it volatilises much more easily. It has a peculiar marine smell, and a rough acrid taste, and is poisonous.

Iodine is sparingly soluble in water, which takes up not more than  $\frac{1}{7000}$  of its weight (1 lb. of water dissolves 1 grain of iodine). The solution has a pretty strong brownish-yellow colour, and the smell of iodine. It dissolves in large quantity, with a deep brown colour, in solution of iodide of potassium, or other soluble iodides, as well as in that of hydriodic acid. Alcohol and ether dissolve iodine abundantly, forming deep-brown solutions. Free iodine, whether in the form of vapour or of solution, gives to starch a deep-blue colour, which affords a very delicate test for iodine, as well as for starch.

Iodine, like chlorine and bromine, enters into combination with phosphorus, metals, &c., when placed in contact with them, and frequently with the phenomena of combustion.

In liquids containing a minute trace of iodine in combination, it is best detected by adding fresh starch rubbed up with water, and then a very little chlorine, which may easily be done by simply inclining over the vessel the mouth of a phial containing some solution of chlorine, but not allowing the liquid to drop. There is always some chlorine gas in the upper part of the phial, which by its weight descends to the surface of the liquid to be tested, and the whole being agitated together, a blue tint, more or less deep, appears if iodine be present. Or oil of vitriol may be added to the liquid supposed to contain iodine, in a phial, and a slip of paper moistened with starch paste inserted between the cork and the neck of the phial, so as to be suspended over the liquid. After a time, if iodine be present, the starch is tinged blue. In both tests the iodine is set free, for combined iodine has no action on starch. In the chlorine test, the superior affinity of chlorine seizes on the metal with which the iodine is united—thus :  $KI + Cl = KCl + I$ .

In power of affinity iodine stands below bromine, as bromine does below chlorine. With metals it forms iodides extremely analogous to the chlorides and bromides. The iodides of lead, mercury, silver, and a few others, are insoluble or sparingly soluble; most of the others are soluble. Some iodides possess beautiful colours, as those of lead and mercury. With hydrogen and oxygen iodine forms compounds, which, as far as they are known, correspond to those of chlorine and bromine with the same elements.

Iodine itself, and many metallic iodides, especially iodide of potassium, are much used in medicine as remedies in scrofula,

and as discutients for glandular tumours in general. They are used both internally and externally in the shape of baths and ointments. Iodide of sulphur is also used medicinally. The long-known efficacy of burnt sponge was shown by Coindet to depend on its containing, as the ashes of sea-plants or zoo-phytes generally do, a small proportion of iodine. The presence of iodine has also been detected in certain mineral springs, both in South America and in Europe, which had acquired celebrity as capable of curing goitre, a disease for which iodine seems to be a specific remedy, at least in all but the most advanced stages. On the whole, the discovery of iodine, which was made almost accidentally by Courtois, a soap-boiler, in Paris, in 1811, has proved a valuable addition to the *Materia Medica*.

## IODINE AND HYDROGEN.

Hydriodic Acid.  $HI = 128.1$ .

This acid, which is exactly similar in properties to hydrochloric and hydrobromic acids, is best obtained in the form of gas, by gently heating a mixture of one part of phosphorus and 16 of iodine, stratified with moistened sand or powdered glass, in a small tube. The gas may be collected over mercury, or absorbed by water, if the liquid acid is required. As iodine and phosphorus act very violently on each other, and indeed take fire in the open air, they ought to be brought in contact

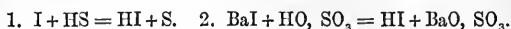


in the retort, or tube, and it is even preferable to fill it first with carbonic acid. Millon has lately proposed another method, namely, to dissolve in a very small quantity of water, in a retort or flask, some iodide of potassium, to add to this as much iodine as it will dissolve, and a moderate quantity of phosphorus in small pieces, and then to apply a gentle heat. In this way the action is more easily regulated. The best proportions are 10 parts of iodide of potassium, 5 of water, 20 of iodine, and 1 of phosphorus. The action is thus explained:  $2KI + I_2 + P + 8HO = HO, 2KO, PO_5 + 7HI$ .

Hydriodic acid gas is transparent, colourless, acid to the taste, and suffocating to the smell. It has a Sp. G. of 4.385, fumes strongly in the air, and is absorbed by water to as great an extent as hydrochloric acid gas, from which it is not to be easily distinguished, except by the action of chlorine or bromine,

which, seizing the hydrogen, disengage the purple vapours of iodine.

The aqueous solution is prepared by passing a current of the gas through water, by passing a current of sulphuretted hydrogen through water in which iodine is suspended, or by adding diluted sulphuric acid to a solution of iodide of barium. The two latter methods are thus expressed :



When very concentrated, this solution acquires a Sp. G. of 1.700. It does not keep well, however, being decomposed by the oxygen of the air, with separation of iodine,  $\text{HI} + \text{O} = \text{HO} + \text{I}$ . With solution of bichloride of platinum, hydriodic acid strikes a deep brownish-red colour ; with nitrate of bismuth a dark brown, nearly black. Hydriodic acid can dissolve a large quantity of free iodine, which gives it a deep brown colour ; hence the gradual decomposition of the acid by the air is shown by its becoming continually darker, from dissolving the iodine separated.

With metallic oxides, this acid forms water and iodides. Thus  $\text{HI} + \text{MO} = \text{MI} + \text{HO}$ . Thus, with solution of silver, it forms a yellowish-white precipitate of iodide of silver ; with solution of lead, a fine yellow precipitate of iodide of lead ; and with solution of peroxide or bichloride of mercury, a beautiful scarlet precipitate of biniodide of mercury. With chlorine and starch, it of course gives the blue iodide of starch.

#### IODINE AND OXYGEN.

a. Iodic Acid.  $\text{IO}_5 = 167.1$ .

Analogous to chloric and bromic acids. To obtain it, iodine is boiled in a long-necked flask with the strongest nitric acid, when it is gradually oxidised, and the excess of nitric acid is expelled by a moderate heat. It may also be obtained by boiling equal parts of chlorate of potash and iodine with 5 parts of water, and a little nitric acid. Iodate of potash is thus formed, which is precipitated as iodate of baryta by adding chloride of barium. Or iodine is suspended in water, through which chlorine is passed till all is dissolved. Soda is added, when some iodine is separated. This is again dissolved by chlorine, and the process repeated till the whole is converted into iodate of soda, which is precipitated by chloride of barium. To obtain the acid from this salt, 9 parts of iodate of baryta are boiled with a mixture of 2 parts of oil of vitriol and 10 or 12

of water. The filtered liquid by evaporation yields iodic acid as a white crystalline solid.

It is very soluble in water and very acid to the taste. It is easily resolved into iodine and oxygen by a red-heat; and it also yields oxygen to many organic substances, and is used as a test for morphia or its salts, which it colours dark brown.

The salts of iodic acid, like the chlorates and bromates, deflagrate with combustible bodies at a red-heat, but not so powerfully as chlorate of potash.

Iodic acid is decomposed, iodine being separated, by hydrochloric and hydrobromic acids, also by sulphuretted hydrogen and sulphurous acid. It may, therefore, be recognised by using any of these re-agents, followed by starch, to detect the free iodine.

With many bases, iodic acid forms several salts; thus with potash it forms an iodate, a biniodate, and a teriodate. It is said also to form basic salts.

b. Periodic Acid.  $\text{IO}_7 = 183.1$ .

Analogous to perchloric acid. Formed when iodate of soda is heated with bleaching liquor (chloride of soda), or when chlorine is passed through a hot solution of 7 parts of dry carbonate of soda in 100 of water, in which 1 part of iodine is suspended, as long as a white crystalline salt is deposited. This is basic periodate of soda,  $2\text{NaO} + \text{IO}_7$ . It is dissolved in dilute nitric acid, and nitrate of lead added, which forms a precipitate of periodate of lead. This last salt is boiled with diluted sulphuric acid, avoiding excess, and the filtered solution on evaporation yields crystals of periodic acid in transparent plates. Or chlorine is passed through a solution of 1 eq. iodate of soda and 3 eq. caustic soda, by which the basic periodate of soda is formed. This salt is precipitated by nitrate of silver. The precipitate, dissolved in boiling nitric acid, deposits, on cooling, neutral periodate of silver; which, when boiled with water, is resolved into the basic periodate, and periodic acid.

When heated, this acid is resolved into oxygen and iodic acid. It forms with bases two series of salts, with 1 and 2 eq. of base.

It is at present doubtful if there exist compounds of iodine with less oxygen than in iodic acid. Salts have been obtained, having a composition represented by  $\text{MO}, \text{IO}$ ; but the supposed hypoiodous acid,  $\text{IO}$ , has not been isolated, and these salts are very easily resolved into a mixture of iodates and iodides, of which they may possibly be, in reality, composed; for  $3(\text{MO}, \text{IO}) = 2\text{MI} + \text{MO}, \text{IO}_5$ .

## IODINE AND NITROGEN.

When iodine is rubbed up with aqua ammoniæ, or an alcoholic solution of iodine is mixed with the same liquid, a velvet black powder is formed, which was long regarded as an iodide of nitrogen  $\text{NI}_3$  or  $\text{NI}_4$ . But it has lately been shown that its true composition is  $\text{NHI}_2$ . It is produced as follows,  $\text{I}_4 + 3 (\text{NH}_3) = 2 (\text{NH}_4\text{I}) + \text{NHI}_2$ . It must be collected on small filters in quantities not exceeding a grain, and allowed to dry spontaneously, the filter, while yet moist, having been spread on a block of wood, or on a brick. I have almost always found it to explode spontaneously at the moment it became quite dry; but it is certain to do so on the slightest touch, and that even when not yet dry. The explosion is very violent, and is attended with a flash of light, though not very bright. From the extreme suddenness of the explosion, it is apt to shatter glass or porcelain vessels, even pretty thick ones, if laid on them.

It is at least possible, that the explosive chloride and bromide of nitrogen may have an analogous constitution; but the difficulty of analysing accurately such dangerous compounds is very great.

It may be observed, in the meantime, that these three explosive bodies are all compounds of nitrogen, and we shall see that many other compounds of nitrogen have this character, such as fulminating silver or fulminating mercury, that is, the fulminates of these metals, detonating gold and silver, which are different, and several metallic nitrets. Even anhydrous nitric acid is explosive.

## IODINE AND CHLORINE.

Iodine readily combines with chlorine, forming apparently two compounds,  $\text{ICl}$  and  $\text{ICl}_3$ , which, however, are not well known. Both of them are volatile, and have an exceedingly pungent odour, strongly affecting the eyes. When acted on by alkalis, they yield iodate of the base and chloride of the metal, while iodine is set free. Water, also, decomposes them. The terchloride forms ruby-red crystals, which sublime spontaneously in the bottle containing them.

## IODINE AND BROMINE.

Iodine appears, also, to form two compounds with bromine, of which one is solid, and the other liquid. With alkalis they

yield a mixture of iodate of the oxide and bromide of the metal, with free iodine.

The facts above briefly indicated concerning chlorine, bromine, iodine, and their compounds, cannot fail to arrest attention, as demonstrating a most wonderful analogy among them, whether in the free state, or when combined with other elements. They form, indeed, a natural and strongly characterised group, and we shall find that groups of three are not unusual among the elements. In the present case, we see, that not only do these three elements agree in their chemical relations, but that their physical properties vary according to a kind of law, by which bromine is always intermediate between chlorine and iodine. Thus chlorine is a gas, bromine a liquid, iodine a solid. Chlorine is the least dense, bromine denser, iodine denser still. Chlorine has the strongest affinities, bromine comes next to it, iodine has the weakest. Chlorine has the lowest atomic weight, iodine the highest, that of bromine is exactly intermediate. And this relation might be traced still further. But when we come to enquire the cause of this graduated resemblance, we find ourselves at a stand. It is not easy to imagine why elementary bodies should exhibit such relations, and as we have no absolute certainty that these bodies are elementary, although we cannot prove them to be otherwise, we may conjecture that they are in reality compounds, containing different proportions of a common element, to which the analogies are due. Dumas has even started the hypothesis, that bromine is formed by the union of the atoms of chlorine and iodine, which agrees perfectly with their relative atomic weights, since the weights of Cl and I are equal to that of 2 Br. But unfortunately for this view, chlorine and iodine do combine and produce, not bromine, but a liquid somewhat like it, chloride of iodine; nor can we extract chlorine or iodine from bromine. On the other hand the relations above enumerated are precisely those which are found to prevail among three contiguous members of what is called a homologous group in organic chemistry. Such a group, as, for example, that of the volatile bases, is so constituted, that each member contains the atoms  $C_2H_2$  in addition to the formula of the member which precedes it. The three first volatile bases are,

|                 |  |
|-----------------|--|
| Methylamine . . | $C_2H_5N$ , which, with $C_2H_2$ , forms       |
| Ethylamine . .  | $C_4H_7N$ , which, again with $C_2H_2$ , forms |
| Propylamine . . | $C_6H_9N$ .                                    |

Now these three compounds, in volatility, density, attractive energy and atomic weight, are related to each other precisely as chlorine, bromine, and iodine. It is, therefore, possible, that

these last may be compounds, members of a homologous series, in which, however, the common difference is not  $C_2 H_2$ , but an unknown value. This is, of course, a mere conjecture, but at present we know of no other principle which can apply to this and other similar groups; while it can only apply to them on the supposition that they are not elementary. It is, however, a general impression among chemists, that chlorine, bromine, and iodine, will one day be found to be compounds.

#### 7. FLUORINE. $F = 18.9$ .

This element occurs in the mineral kingdom combined with calcium, as fluor-spar; also in small proportions as an element of mica, of topaz, and of some other minerals. One remarkable mineral, cryolite, is a compound of fluoride of aluminium and fluoride of sodium. Fluoride of calcium is also in minute quantity an ingredient of animal bones, especially of the enamel of the teeth, and of the urine of some animals. It is very remarkable, that fossil bones contain much more fluoride of calcium than recent bones; in some cases even 10 per cent. Even human bones of the historical period, as bones from the tombs of Egypt, or from Pompeii, appear to contain more fluoride of calcium than those of the present day. Dr. Wilson has found traces of fluoride of calcium in almost all rocks and waters, including sea-water, and also in most animal and vegetable substances.

Fluorine has not yet been isolated, owing, no doubt, to its very powerful affinities, which cause it, even if separated from one substance, instantly to unite with another, derived from the substance of the vessel used for the experiment. Its properties, in the separate state, are therefore unknown. Knox and Baudrimont have, of late, made repeated efforts to isolate fluorine, using vessels of fluor-spar, &c., but as yet without satisfactory results; although it is conjectured, from some of these experiments, to be a yellow gas, not unlike chlorine. It is probable, however, that the presence of chlorine has been the cause of this apparent resemblance.

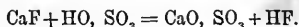
The affinities of fluorine for metals, and for electro-positive elements in general, are very powerful indeed; probably surpassing those of oxygen. On the other hand, it has not been obtained in combination with any of the more negative elements, such as oxygen, chlorine, bromine, and iodine. These considerations render it probable that it is a highly negative body; and the character of its compounds with hydrogen and metals indicates a strong analogy between fluorine and chlorine, bromine, and iodine.



## FLUORINE AND HYDROGEN.

Hydrofluoric acid.  $\text{HF} = 19.9$ .

**SYN. Fluoric acid.**—This acid is obtained by the action of oil of vitriol on fluoride of calcium (fluor-spar). The powdered mineral is gently heated with the acid in a retort of lead, silver, or platinum (see figure), as glass and porcelain are destroyed by the process, and the acid condensed in a receiver of the same metal, surrounded by a freezing mixture. The action is thus expressed—



The acid appears as a very volatile liquid, strongly acid and corrosive, fuming in the air.

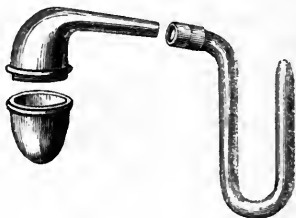
A drop on the skin burns it like red-hot iron, and causes a painful sore, not easily healed. Even the vapours, if they are allowed to come much in contact with the hand, are apt to cause painful sores under the nails. The acid, even when much diluted, or in the form

of vapour, rapidly corrodes glass, and may be used for etching on glass plates.

The liquid acid, as above prepared, was supposed to be anhydrous; but has lately been ascertained to contain water, which may be removed by an excess of anhydrous phosphoric acid, or the compound of hydrofluoric acid with fluoride of potassium,  $\text{HF}, \text{KF}$ , may be heated, and the vapours condensed in a tube of metal placed in a freezing mixture. The anhydrous acid is very mobile and volatile, and acts but slowly on glass.

With metallic oxides, hydrofluoric acid gives rise to water and metallic fluorides;  $\text{HF} + \text{MO} = \text{HO} + \text{MF}$ . The affinity of fluorine for silicon is such, that hydrofluoric acid decomposes all silicious compounds; and this explains its corrosive action on glass and porcelain. Berzelius has employed this acid as a means of analysing silicious minerals. As the fluoride of silicon is gaseous, any such mineral, if digested with hydrofluoric acid, soon loses all its silica, and is dissolved, so that the other ingredients may be determined.

Many metallic acids, such as titanio, columbic, tungstic and molybdic acids, yield, with hydrofluoric acid, water, and new



acids, composed of hydrofluoric acid, with the fluoride of the metal. Thus titanous acid acts on it as follows, yielding fluotitanous acid,  $\text{TiO}_2 + 3\text{HF} = 2\text{HO} + (\text{HF}, \text{TiF}_3)$ . Such compound acids act on metallic protoxides, exchanging hydrogen for metals, and producing double salts, such as fluotitanate of potash,  $\text{KF} + \text{TiF}_3$ . Hydrofluoric acid acts in a similar way on silicic and boracic acids.

No compound of fluorine with any of the preceding elements, except hydrogen, is yet known. Its compounds with silicon, boron, and the metals will come to be described in their natural places.

#### 8. SULPHUR. S = 16.

Sulphur occurs, especially in volcanic districts, in a state of purity, often crystallised. It is also found in combination with oxygen, as sulphuric acid, in gypsum, heavy spar, and many other minerals, with hydrogen as sulphuretted hydrogen, in mineral waters, and above all with metals, most abundantly with lead, iron, copper, &c., &c. Finally, it is an essential ingredient of vegetable and animal fibrine, albumen, and caseine, and as such is indispensable to vegetation and to animal life. Some essential oils, such as those of mustard, of horse-radish, of assafoetida, &c. contain a large proportion of sulphur.

Native sulphur is purified by sublimation, when the sulphur assumes the form of a fine light powder, flowers of sulphur. It also occurs in cylindrical sticks, roll sulphur, which has been melted and run into moulds.

Sulphur is a solid of a pale-yellow colour, of Sp. G. 1.99, and when pure has neither taste nor smell. It melts at  $226^\circ$  and boils at  $600^\circ$ , yielding a deep brownish-yellow vapour, or gas. At temperatures below  $390^\circ$ , the melted sulphur is very fluid, but if heated to and beyond that point, it becomes so thick and viscid that it cannot be poured out of the vessel. If the heat be still increased, so as to approach the boiling point of sulphur, it again becomes fluid, although not so much so as at  $230^\circ$  or  $240^\circ$ . If now allowed gradually to cool, it first becomes thick, and on cooling still further, quite fluid again. When thrown into water in its most fluid state (at  $240^\circ$ ), it instantly becomes a hard brittle yellow mass; but if heated to between  $500^\circ$  and  $600^\circ$  for some time, and then poured into water in a slender stream, it remains brown and transparent, and is so flexible that it may be kneaded in the fingers, and drawn into threads. Melted sulphur may be used for taking copies of reliefs or intaglios, for if poured into a mould while in its most fluid state it takes very sharp impressions in solidifying. In the viscid or plastic

state it cannot be long kept, as it gradually becomes yellow and crystalline.

Sulphur is a very bad conductor of heat and of electricity, hence it becomes strongly electric by friction. It crystallises in two distinct and irreconcilable forms, probably from a difference of temperature; from a solution in bisulphide of carbon, or chloride of sulphur, in acute rhombic octohedrons; and when melted and allowed to cool, in oblique rhombic prisms. It is thus dimorphous, and besides occurs in an altogether amorphous, viscid state when heated to  $500^{\circ}$  and thrown into cold water.

These three states of sulphur are called different allotropic modifications of that element, as has been mentioned under Allotropism. The natural crystals of sulphur, which are the same rhombic octohedrons as those deposited from bisulphide of carbon, constitute the first allotropic variety, *Sa*. It is nearly transparent, of a bright amber yellow, permanent in the air; it has a density of 2.05, and melts at  $239^{\circ}$ . The prismatic crystals obtained by the cooling of melted sulphur are the second variety, or *Sβ*. It has, when first formed, a brownish yellow colour, and if kept some time becomes opaque and friable, the crystals splitting up into small rhombic octohedrons. It melts at  $248^{\circ}$ , and has a density of 1.98, which is that of the yellow roll sulphur. The viscid form is the third allotropic state or *Sγ*. Its colour varies from deep amber yellow to dark brown, and is darker the higher the temperature at which it has been formed. Its melting point is not ascertained, its density is only 1.957, *Sa* and *Sβ* are easily soluble in bisulphide of carbon, with the aid of heat; *Sγ* does not dissolve in that liquid. It is probable that these three states depend on variations in the arrangement of the molecules, or of the number of ultimate atoms grouped to form a molecule. They differ in density, and the three liquid states above described are possibly the liquid states corresponding to the three solid ones; while there is even some reason to think that a similar difference may be traced in the gaseous form, at least in some of its compounds, in which the vapour of sulphur must occupy only  $\frac{1}{8}$  of the space occupied by the equivalent weight of hydrogen, if we suppose it to have the density of the common vapour of sulphur, which is 6.654. As it is much more probable that in sulphuretted hydrogen gas, equal volumes of the elements are combined, it is probable that the density of the vapour of sulphur as it exists in that compound is  $\frac{1}{8}$  of the above, or 1.109.

Magnus has described two other forms of sulphur, one red, the other black, probably allotropic. The black sulphur is insoluble in bisulphide of carbon.

Sulphur is insoluble in water, soluble in alcohol, ether, and oils, also in bisulphuret of carbon and in chloride of sulphur.

The affinities of sulphur are powerful; it forms numerous and important compounds, especially those with oxygen, hydrogen, and the metals. With many metals it combines when heated along with them, the combination being accompanied with the development of heat and light. In other words, metals undergo combustion with sulphur, just as with oxygen or chlorine. The compounds of sulphur with metals are called sulphurets or sulphides.

Besides roll sulphur, and sublimed sulphur, there is another form, namely, precipitated sulphur or lac sulphuris. This is a light powder, nearly white, obtained by boiling sulphur with water and an alkali, and adding an acid to the solution, when sulphur separates as a precipitate. It is very finely divided, and appears to contain some water, although not perhaps chemically combined.

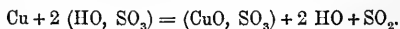
Sulphur is much used both externally and internally in medicine. It is a mild laxative, and acts as a specific when employed as ointment in prurigo and some other cutaneous affections.

When heated to above  $560^{\circ}$  in the open air, sulphur takes fire and burns with a blue flame, producing a very suffocating gas, which is sulphurous acid, the only compound of sulphur with oxygen capable of being formed by direct combination of its elements. There are, however, several other compounds of sulphur and oxygen, and one of them, sulphuric acid, is perhaps the most important agent possessed by the chemist.

#### SULPHUR AND OXYGEN.

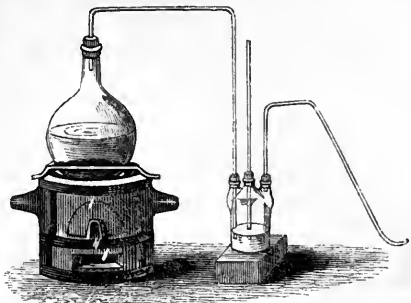
##### a. Sulphurous Acid. $\text{SO}_2 = 32$ .

This is the gas produced when sulphur burns in the air or in oxygen gas. It is best obtained pure by heating oil of vitriol with mercury or copper as in the figure. Either of these metals deprives a part of the sulphuric acid of oxygen, and the oxide thus formed combines with the rest of the acid. Thus—



The gas, after being passed through a bottle with a little water, to wash it, may be collected over mercury, being absorbed by water. It may also be obtained by heating sulphur with peroxide of manganese, or charcoal with sulphuric acid. In the latter case it is mixed with carbonic acid, but this is of no moment, when the sulphurous acid is used to form the sulphites, the carbonic acid being expelled.

Sulphurous acid is a transparent and colourless gas ; it has a peculiar disagreeable taste, and a most suffocating smell, and is very injurious when respired, its effects, such as hard cough, constriction in the trachea, &c., continuing for a long time. The spasmodic constriction of the glottis produced by it is at once relieved by inhaling a little ether or chloroform.



It is also very injurious to vegetation. Its Sp. G. is 2.222, that is, double that of oxygen. When sulphur burns in oxygen, so as to form this gas, the volume remains unchanged, while the weight is doubled. This proves that 1 eq. of sulphur = 16 combines with 2 eq. of oxygen, also = 16. It bleaches organic matters, such as flowers, without destroying the colouring matter as chlorine does ; for the addition of a stronger acid produces the same red as if the colour had not been bleached. Sulphurous acid gas is liquefied by intense cold, and yields a very volatile liquid. The liquid acid is obtained by causing the dry gas to pass through a metallic worm, placed in a freezing mixture of salt and snow, and communicating with a receiver, also cooled. It may then be sealed in small tubes, when it exerts, at 60°, a pressure of about  $2\frac{1}{2}$  atmospheres. It boils, under the ordinary pressure, at 17.5°, and is solidified by a cold of — 105°.

Water absorbs about 50 times its volume of this gas, forming liquid sulphurous acid, as it is called, properly an aqueous solution of the acid. This solution has the suffocating smell, peculiar taste, and bleaching properties of the gas. If exposed to the air, it gradually absorbs oxygen, and passes into sulphuric acid. Nitric acid also converts sulphurous acid into sulphuric acid.

With bases, sulphurous acid forms salts which are called sulphites. They have all the unpleasant taste of the acid, and when acted on by stronger acids, give off the suffocating smell of burning sulphur. These salts, as well as the acids, are occasionally used by the chemist as deoxidising agents, the sulphurous acid having a very powerful attraction for a third eq. of oxygen to form sulphuric acid. The oxides of mercury, silver,

gold, and platinum, in solutions of their salts, are reduced to the metallic state by sulphurous acid.

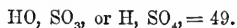
b. Anhydrous Sulphuric Acid.  $\text{SO}_3 = 40$ .

The formula  $\text{SO}_3$  represents dry or anhydrous sulphuric acid, or at least a substance having the composition of oil of vitriol, *minus* 1 eq. of water. But it is very doubtful if this compound really possesses acid properties; and we consider as true sulphuric acid the well-known compound oil of vitriol, which may be viewed either as a compound of water (a hydrate), or a compound of hydrogen (a hydrogen acid, analogous to hydrochloric acid).

Anhydrous sulphuric acid is obtained by distilling dried basic persulphate of iron,  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_3$ , when the peroxide of iron is left, and sulphuric acid distils over, condensing in the receiver (if kept dry) as a fuming acid, called the acid of Nordhausen. It is a solution of anhydrous acid in oil of vitriol, and when gently heated, yields the anhydrous acid, which is very volatile, and which condenses as a white crystalline solid, which gives off thick fumes in moist air, is converted into vapour at about  $110^\circ$ , and has so strong an affinity for the elements of water, that when thrown into water it hisses as a red-hot iron would do, combining with the water, and forming oil of vitriol. According to Marignac, the anhydrous acid exists in two forms, one of which melts at  $65^\circ$ , the other some degrees below  $212^\circ$ .

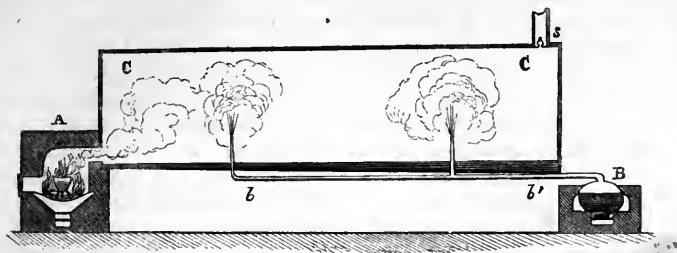
This compound,  $\text{SO}_3$ , enters into few combinations, and does not form the ordinary sulphates, unless the elements of water be present. Its claim to the character of an acid is therefore doubtful, and depends on the view which makes oil of vitriol a hydrate,  $\text{HO}$ ,  $\text{SO}_3$ . It dissolves sulphur, forming a blue, green, or brown solution, as the amount of sulphur is small or large. It also dissolves iodine, and forms with  $\frac{1}{10}$  of its weight of that element a green crystalline compound.

c. OIL OF VITRIOL, OR TRUE SULPHURIC ACID.



This acid cannot be formed by the direct union of its elements, but is produced by causing sulphurous acid to unite with an additional eq. of oxygen, in contact with the elements of water. Sulphur is burned with the aid of nitrate of potash or soda, thus yielding a mixture of sulphurous acid and nitrous acid gases. These gases are conducted into leaden chambers along with atmospheric air and steam, the bottom of the chambers being covered with water. (See the figure.) All the changes

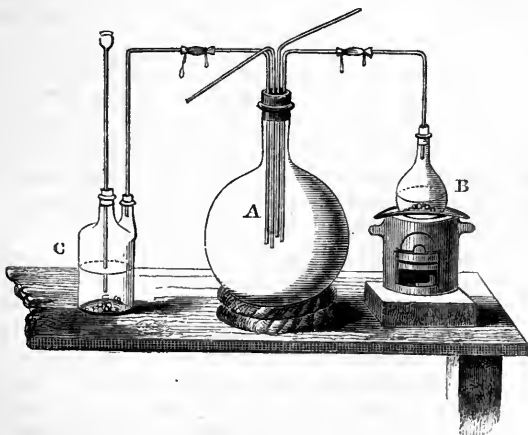
which take place are not thoroughly understood ; but this much is certain, that the sulphurous acid is oxidised at the expense



of the nitrous acid, reducing it to the state of deutoxide of nitrogen.

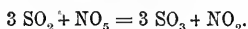


The water becomes gradually charged with oil of vitriol, and the deutoxide of nitrogen, being reconverted into nitrous acid by contact with the oxygen of the air, again yields half its oxygen to a fresh portion of sulphurous acid ; and thus, for an indefinite period, acts as a carrier of oxygen from the air to the sulphurous acid. In this way, a comparatively small quantity of nitrate is required for a large quantity of sulphur. The



process may be illustrated on the small scale by means of the apparatus here figured. A is a large balloon, the inside of which is moist ; B, an apparatus for producing sulphurous acid

gas ; and c, one in which deutoxide of nitrogen is formed. For this we may substitute a retort in which nitric acid and starch, heated together, yield nitrous acid. The deutoxide, with the oxygen of the air in the balloon, forms nitrous acid, which, with the sulphurous acid, and water, forms a crystalline substance, containing the elements of these three bodies. This is decomposed by the excess of water, yielding sulphuric acid, the sulphurous acid being oxidised at the expense of the nitrous acid, and deutoxide of nitrogen, which again forms nitrous acid with the oxygen of the air of the balloon, or with oxygen introduced by one of the lateral tubes, and thus is again ready to unite with another portion of sulphurous acid, and so on. The water in the balloon soon becomes strongly charged with sulphuric acid. The formation of the crystals is not essential, and chiefly depends on the fact that too little water is present. When there is enough of water, the nitrous acid is changed into nitric acid and deutoxide of nitrogen, and the nascent nitric acid oxidises the sulphurous acid as above. The action of nitric acid on sulphurous acid is as follows :



and that of nitrous acid has already been explained.

The nature of the crystals above mentioned is not satisfactorily ascertained. Rose considers them as composed of  $\text{NO}_2$ ,  $2 \text{ SO}_3$ , which explains their decomposition by water, yielding sulphuric acid and deutoxide of nitrogen. De la Provostaye regards them as  $\text{SO}_3 + \text{SO}_2 + \text{NO}_4$  ; while others conceive their composition to be  $2 \text{ SO}_2 + \text{NO}_4 + \text{HO}$ . In the latter case, when acted on by water, they would yield  $2 \text{ SO}_3 + \text{NO}_2 + \text{HO}$ , which agrees with Rose's view, so far as the result is concerned. In practice this is a question of little importance, because, if water be duly supplied, the crystals do not appear, being decomposed as fast as produced, and the essential points are, a due proportion of sulphurous acid, of nitrous acid, of water, and of air. The gases which escape from the chambers consist of atmospheric nitrogen and deutoxide of nitrogen ; and to avoid the loss of the latter, which, as has been shown, serves as a carrier of oxygen, and in this way to diminish the amount of nitre required for burning with the sulphur, Gay Lussac proposed to cause the escaping gases to pass through a kind of chimney, filled with bits of coke, through which oil of vitriol is slowly made to trickle. The oil of vitriol absorbs the deutoxide, and is brought in contact with the sulphurous acid near the entrance of the chambers. In this way, it is said, the quantity of nitre required has been diminished one half.



When the liquid has become very acid, and has acquired a Sp. G. of 1.45, beyond which it must not be carried in the lead chambers, it is boiled down, first in leaden pans, afterwards in platinum or glass vessels, until it acquires the Sp. G. 1.845, when it begins to be converted into vapour itself, all the superfluous water being now driven off. The remaining liquid is now oil of vitriol.

Oil of vitriol, or hydrated sulphuric acid, is an oily liquid, nearly twice as heavy as water, very acid and corrosive, charring all organic matters, apparently by its very strong attraction for water, or its elements. It freezes at  $-31^{\circ}$ , and boils at  $617^{\circ}$ .

The oil of vitriol prepared at Nordhausen and other places, by the old process of distilling partially dried green vitriol (whence its name), fumes on exposure to the air, and is called Nordhausen oil of vitriol, or fuming sulphuric acid. It is, in fact, a compound of 1 eq. of anhydrous acid, and 1 eq. of common or hydrated sulphuric acid =  $\text{HO}$ , 2  $\text{SO}_3$ , or  $\text{HO}$ ,  $\text{SO}_3$  +  $\text{SO}_3$ . Its Sp. G. is 1.9. When the fuming acid of Nordhausen is distilled at about  $290^{\circ}$ , anhydrous acid distils over, and hydrated acid remains behind. Most specimens of the fuming acid contain 5 to 8 per cent of hydrated acid, in excess beyond the formula  $\text{HO}$ ,  $\text{SO}_3$  +  $\text{SO}_3$ .

If we view common sulphuric acid as a hydrate of the anhydrous acid, then we have several hydrates, of which the fuming acid is one. There are, 1st, fuming acid,  $\text{HO}$ , 2  $\text{SO}_3$ ; 2nd, common acid,  $\text{HO}$ ,  $\text{SO}_3$ ; 3rd,  $\text{HO}$ ,  $\text{SO}_3$  +  $\text{HO}$  =  $\text{SO}_3$  + 2  $\text{HO}$ ; 4th,  $\text{HO}$ ,  $\text{SO}_3$  + 2  $\text{HO}$  =  $\text{SO}_3$  + 3  $\text{HO}$ .

The third hydrate has a Sp. G. of 1.78, and at  $-39^{\circ}$  crystallizes in large regular transparent crystals. Of the two eqs. of water it contains, one is easily replaced by an eq. of a neutral salt; thus  $\text{HO}$ ,  $\text{SO}_3$  +  $\text{HO}$  gives rise to bisulphate of potash ( $\text{HO}$ ,  $\text{SO}_3$  +  $\text{KO}$ ,  $\text{SO}_3$ ), when the 2nd eq. of water is replaced by neutral sulphate of potash. The first eq. of water can only be displaced by an eq. of a base; as when  $\text{HO}$ ,  $\text{SO}_3$  gives rise to neutral sulphate of potash,  $\text{KO}$ ,  $\text{SO}_3$ .

The fourth hydrate may be regarded as the third + 1 eq. water of crystallisation. Its Sp. G. is 1.632. If heated to  $212^{\circ}$ , it loses water, until nothing remains but the third hydrate.

If we view oil of vitriol,  $\text{HO}$ ,  $\text{SO}_3$ , as the original compound from which all the others are derived, then the fuming acid will be a compound of 1 eq. of it with 1 eq. of anhydrous acid, and the other two hydrates will contain 1 eq. oil of vitriol, with 1 and 2 eq. of water respectively.

The attraction of oil of vitriol for water is very strong. When

these liquids are mixed, a great amount of heat is developed, depending partly on the energetic chemical action, partly on the condensation which takes place ; for the volume of the diluted acid, after cooling, is found to be considerably less than that of the acid and water before mixture. Oil of vitriol attracts moisture strongly from the atmosphere, becoming rapidly weaker if exposed. This property is made use of in Leslie's ingenious method of freezing water in vacuo by its own evaporation ; the evaporation being greatly hastened by the presence of a vessel containing oil of vitriol, to absorb the vapour as fast as it is formed. In chemical researches, where heat is to be avoided, liquids are frequently concentrated by being placed either in vacuo, or simply under a bell-jar, along with a basin of this acid. Many gases, such as chlorine, carbonic acid, &c. &c., are most conveniently deprived of moisture by causing them to pass through oil of vitriol, which arrests all the water they contain, or by passing them through one, two, or more U-shaped tubes, filled with fragments of pumice moistened with oil of vitriol. In this way the last traces of moisture can be removed. It is this powerful attraction for water that is the principal cause of the charring or corrosion of organic matters by this acid. When wood, for example, is charred by sulphuric acid, the acid is found to have undergone no further change, except that it is more diluted, having combined with water, the elements of which are derived from the wood. Now, as wood may be represented as carbon + water, the removal of water is, of course, accompanied by a separation of carbon.

No chemical agent is applied to a greater number of purposes in the useful arts than sulphuric acid ; and hence its manufacture is of very high importance. Since the introduction and improvement of the process now followed, the price of this valuable product has been diminished to a trifling fraction of what it was ; and its applications have in consequence become vastly more numerous and important. These will be described in their proper places ; but it may here be mentioned, that two of the most extensive and valuable chemical manufactures, those of soda from sea-salt, and of bleaching-powder, are entirely dependent on the supply of sulphuric acid at a low price ; and that not only these manufactures have benefited by every reduction in the cost of making the acid, but also all the important arts to which soda and bleaching-powder are essential ; such as soap-making, glass-making, the cotton and calico-printing trades, as well as the manufacture of nitric and hydrochloric acids, and that of phosphorus, or of superphosphate of lime from bones.

The uses of this acid to the scientific chemist are innumerable ; almost every page of chemical works bears evidence of this. In medicine, diluted sulphuric acid is used as a styptic and refrigerant, and care should be taken to avoid administering it along with incompatible substances, such as all bases, and many salts.

The commercial acid is never pure. The chief impurities are sulphate of lead, derived from the lead chambers ; arsenic, and occasionally selenium, derived from the sulphur ; and nitrous, or hyponitrous acid. It is purified by distillation, the first portions being rejected, as containing the nitrous acid. The operation in glass vessels requires caution, as from the high temperature, and the tendency of the acid to boil with succussions, the retorts are liable to be broken. The danger is best avoided by introducing into the retort some coils of platinum wire, and heating from the sides, so that the ebullition may go on at the surface chiefly, as in the figure. The cap, A, being put over



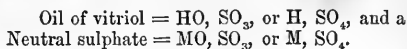
the upper part of the retort, greatly accelerates the distillation, by preventing the vapour from condensing there and falling back into the body of the retort.

The pure distilled acid is perfectly colourless, and, when cold, devoid of smell ; it ought also to be entirely dissipated when heated on platinum, leaving no residue.

The presence of sulphuric acid, whether free or combined, is detected in solutions by the characteristic property of forming, with any soluble compound of barium, a precipitate of sulphate of baryta, which is not only insoluble in water, but also in the strongest acids.

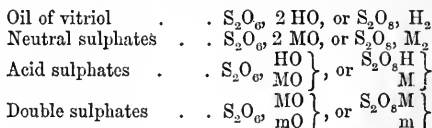
With bases sulphuric acid forms salts, which are called sulphates. In the neutral sulphates, the water of the oil of vitriol is replaced by its equivalent of a metallic oxide ; or, if we regard oil of vitriol as a hydrogen acid, then in the neutral sulphates

the hydrogen is replaced by its equivalent of metal. Thus we have



The acid in the neutral sulphates, as may be seen by their formulæ, contains three times as much oxygen as the base by which it is neutralised. This holds true also in the sulphates of sesquioxides, the formula of which is  $\text{M}_2\text{O}_3$ ,  $3 \text{SO}_3$ , or  $\text{M}_2$ ,  $3 \text{SO}_4$ . The acid sulphates, which are numerous, contain twice as much acid as the neutral; thus acid sulphate, or bisulphate of potash, is  $\text{KO}, \text{HO}, 2 \text{SO}_3$ ; here the acid contains six times as much oxygen as the alkaline base.

From the great tendency of sulphuric acid to form acid and double salts, it is now often regarded as a bibasic acid. On this view, its formula is doubled, and we have for



The double sulphates here alluded to are those which contain two metallic protoxides, such as the sulphate of potash and magnesia,  $\text{KO}, \text{SO}_3 + \text{Mg SO}_3 + 6 \text{ aq.}$ , or, on the bibasic hypothesis  $\text{S}_2\text{O}_6 \left\{ \begin{array}{l} \text{KO} \\ \text{Mg.O} \end{array} \right\} + 6 \text{ aq.}$ , or,  $\text{S}_2 \text{O}_8 \left\{ \begin{array}{l} \text{K} \\ \text{Mg} \end{array} \right\} + 6 \text{ eq.}$  They are all isomorphous.

But sulphuric acid, besides forming a numerous series of such double salts, yields many of a totally different type, namely, of the type of alum, in which there are present, to 1 eq. of a sulphate of a protoxide, 1 eq. of a neutral sulphate (tersulphate) of sesquioxide. Thus, alum is  $\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3 \text{SO}_2 + 24 \text{ aq.}$ ; or the general formula is  $\text{MO}, \text{SO}_3 + \text{m}_2\text{O}_3, 3 \text{SO}_3 + 24 \text{ aq.}$ ; in which M is a metal, such as potassium, sodium, or ammonium, while m is a metal of the group aluminium, iron, manganese and chromium. The 12 alums thus constituted all exist, and are isomorphous, crystallising in octohedrons. Two of them, common alum, above mentioned, and ammonia alum, in which the potash of common alum is replaced by oxide of ammonium, are of great value in the arts.

There are also a few basic sulphates, such as that of copper,  $3 \text{ Cu O} + \text{SO}_3 + 2 \text{ aq.}$

The affinity of sulphuric acid for most bases is stronger than that of all other acids. At a red-heat, phosphoric and boracic acids, being fixed in the fire, expel sulphuric acid from its salts.

In solution, sulphate of lime is decomposed by oxalic and racemic acids, which seize the lime ; and sulphate of potash, by tartaric, racemic, and perchloric acids, which combine with the potash. In other circumstances, however, the sulphuric acid appears stronger than the acids just mentioned : thus, it decomposes phosphates in the cold, and tartrates, or perchlorates, with the aid of a gentle heat. An interesting instance of the modifying influence of changed conditions occurs in the case of sulphate of baryta. If, on the one hand, that salt be boiled for some time with considerable excess of an alkaline carbonate, carbonate of potash for example, a large quantity of the sulphate will be changed into the carbonate of baryta ; while, on the other hand, if this carbonate of baryta be boiled in a similar manner, but with *sulphate* of potash, it will reproduce the original sulphate of baryta.

Many sulphates of metallic oxides, when exposed to a red-heat along with charcoal, or in a current of hydrogen gas, lose all the oxygen they contain, and are changed into sulphurets of the metal. When charcoal is used, the oxygen escapes as carbonic oxide, or carbonic acid gas ; when hydrogen is employed, the oxygen is given off as water. Thus,  $\text{MO}, \text{SO}_3 + \text{C}_4 = 4 \text{CO} + \text{MS}$  ; or  $\text{MO}, \text{SO}_3 + \text{H}_4 = 4 \text{HO} + \text{MS}$ .

d. Hyposulphurous Acid.  $\text{S}_2\text{O}_2 = 48$ .

This acid is unknown in the separate state. Its salts are formed when sulphur is boiled with a solution of sulphite. Thus if sulphite of soda is boiled with sulphur, we have  $\text{NaO}, \text{SO}_2 + \text{S} = \text{NaO}, \text{S}_2\text{O}_2$ . The salts of this acid are called hyposulphites, and they are all except the hyposulphite of baryta, easily soluble in water. Hyposulphites are also formed when alkalies are fused at a low heat with sulphur, and when solutions of alkaline sulphurets are exposed to the air so as to be slowly oxidised.

When we attempt to separate hyposulphurous acid from any of its salts, it is instantly resolved into sulphurous acid and sulphur,  $\text{S}_2\text{O}_2 = \text{SO}_2 + \text{S}$ . When oxidised by nitric acid, the hyposulphites are converted into bisulphates,  $\text{KO}, \text{S}_2\text{O}_2 + \text{O}_4 = \text{KO}, 2 \text{SO}_3$ .

This acid, and all its soluble salts, possess the remarkable property of dissolving all the compounds of silver, even the chloride, which is insoluble in the strongest acids ; and the solution thus formed has a very intense sweet taste, with a metallic after-taste. This property has been made available in photography, for the purpose of dissolving the sensitive coating of iodide from the plate of silver, or of chloride, bromide

or iodide from sensitive paper, after exposure to light, and thus fixing the image already formed. For this purpose hyposulphite of soda is now prepared in considerable quantity.

e. Hyposulphuric Acid.  $S_2O_5 = 72$ .

This acid is formed, along with sulphuric acid, when sulphurous acid is oxidised by means of peroxide of manganese;  $3 SO_2 + 2 MnO_2 = MnO, S_2O_5 + MnO, SO_3$ . The solution thus obtained is decomposed by baryta, or by sulphuret of barium, by which the manganese is separated as oxide or as sulphuret, and the sulphuric acid as sulphate of baryta, and hyposulphate of baryta, a soluble salt, is obtained;  $MnO, S_2O_5 + BaS = BaO, S_2O_5 + MnS$ ; and  $MnO, SO_3 + BaS = BaO, SO_3 + MnS$ . The filtered solution is then mixed with just as much diluted sulphuric acid as is sufficient to separate the baryta as the insoluble sulphate, and the liquid now contains hyposulphuric acid;  $BaO, S_2O_5 + HO, SO_3 = BaO, SO_3 + HO, S_2O_5$ .

When concentrated by evaporation in vacuo, hyposulphuric acid forms a syrupy liquid of a very acid taste, and devoid of smell. When heated, it yields sulphurous acid gas, while sulphuric acid remains,  $S_2O_5 = SO_2 + SO_3$ . Its salts, when ignited, give off sulphurous acid, while sulphates remain;  $MO, S_2O_5 = SO_2 + MO, SO_3$ .

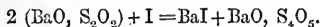
With bases, this acid forms salts, most of which crystallise with great facility. It is not applied to any useful purpose.

f. Trithionic Acid.  $S_3O_5 = 88$ .

Discovered by Langlois. When bisulphite of potash is digested along with sulphur and water, without boiling, a salt is gradually produced, which contains this new acid. The acid may be isolated by means of perchloric acid, which removes the potash. It forms an acid liquid, which is slowly decomposed, and when heated is resolved into sulphurous acid, sulphur, and sulphuric acid; for  $S_3O_5 = SO_2 + S + SO_3$ . The theory of its formation is not yet fully understood, and the acid itself is as yet but little known. The salt which it forms with potash crystallises easily, and when heated yields sulphurous acid, sulphur and sulphate of potash;  $KO, S_3O_5 = SO_2 + S + KO, SO_3$ .

g. Tetrathionic Acid.  $S_4O_5 = 104$ .

Discovered by Fordos and Gelis. When iodine is dissolved in the solution of a hyposulphite, as hyposulphite of soda or baryta, the following change takes place:



Here 2 eq. of hyposulphite of baryta and 1 eq. of iodine yield 1 eq. of iodide of barium and 1 eq. of the baryta-salt of the new acid. Alcohol dissolves the former, and leaves the latter pure. By the cautious addition of diluted sulphuric acid, the baryta is precipitated, and the new acid is obtained dissolved in water. It resembles the two preceding acids, and, like the last, it is resolved, when heated, into sulphurous acid, sulphur, and sulphuric acid,  $S_4O_5 = SO_2 + S_2 + SO_3$ . Here the quantity of sulphur separated is exactly double of that yielded by the acid last described.

The salts of this acid crystallise, and when heated yield 1 eq. of sulphurous acid, 2 eqs. of sulphur, and 1 eq. of sulphuric acid;  $MO, S_4O_5 = SO_2 + S_2 + MO, SO_3$ .

#### h. Pentathionic Acid. $S_5O_5 = 120$ .

This acid is formed when sulphuretted hydrogen is passed through a solution of sulphurous acid, when sulphur is deposited.  $5 SO_2 + 5 HS = S_5O_5 + 5 HO + S_5$ . The new acid is very unstable, but if neutralised by baryta, the pentathionate of that base may be obtained in silky scales. It has no special interest, and resembles the preceding acids.

The following table exhibits the composition of the compounds of sulphur and oxygen above described, with their formulæ, and those of their neutral salts, according to the older and newer views of the constitution of acids.

|  | Older View.                       |                                   | New View.                        |                                  |
|--|-----------------------------------|-----------------------------------|----------------------------------|----------------------------------|
|  | Acids.                            | Salts.                            | Acids.                           | Salts.                           |
| Sulphurous Acid . .                    | HO, SO <sub>2</sub>               | MO, SO <sub>2</sub>               | H, SO <sub>3</sub>               | M, S O <sub>3</sub>              |
| Sulphuric Acid . .                     | HO, SO <sub>3</sub>               | MO, SO <sub>3</sub>               | H, SO <sub>4</sub>               | M, S O <sub>4</sub>              |
| Hyposulphurous Acid .                  | HO, S <sub>2</sub> O <sub>2</sub> | MO, S <sub>2</sub> O <sub>2</sub> | H, S <sub>2</sub> O <sub>3</sub> | M, S <sub>2</sub> O <sub>3</sub> |
| Hyposulphuric or di-thionic Acid . . } | HO, S <sub>2</sub> O <sub>5</sub> | MO, S <sub>2</sub> O <sub>5</sub> | H, S <sub>2</sub> O <sub>6</sub> | M, S <sub>2</sub> O <sub>6</sub> |
| Trithionic Acid . .                    | HO, S <sub>3</sub> O <sub>5</sub> | MO, S <sub>3</sub> O <sub>5</sub> | H, S <sub>3</sub> O <sub>6</sub> | M, S <sub>3</sub> O <sub>6</sub> |
| Tetrathionic Acid . .                  | HO, S <sub>4</sub> O <sub>5</sub> | MO, S <sub>4</sub> O <sub>5</sub> | H, S <sub>4</sub> O <sub>6</sub> | M, S <sub>4</sub> O <sub>6</sub> |
| Pentathionic Acid . .                  | HO, S <sub>5</sub> O <sub>5</sub> | MO, S <sub>5</sub> O <sub>5</sub> | H, S <sub>5</sub> O <sub>6</sub> | M, S <sub>5</sub> O <sub>6</sub> |

Now, when we reflect that all the salts in the above table although containing only 1 eq. of metal or of base, are neutral while the acids, according to the older view, and considered as oxygen compounds, contain different proportions of oxygen, we can hardly hesitate to prefer the newer view, according to which all true acids are hydrogen compounds, and their capacity of saturation, or power of neutralising bases, depends, not on the oxygen they contain, but on the amount of hydrogen re-

placeable by metals, which in all these acids, is 1 equivalent. This at once accounts for the fact that acids so different in composition should all form neutral salts with the same quantity of base. The difference lies in the compound radicals, which according to this theory, are united with hydrogen in the acids, and the composition of which may vary *ad infinitum* without affecting the neutralising power, provided the replaceable hydrogen continue unaltered. In fact, an acid has been described by Regnault in which 1 eq. of chlorine is added to the radical of sulphurous acid; and another by Pelouze, in which 1 eq. of deutoxide of nitrogen is added to the same radical, without affecting the power of neutralisation.

If we take the radical of sulphurous acid as the first member of the series, all the above acids may be thus represented:—

|                      |       |                            |
|----------------------|-------|----------------------------|
| Sulphurous Acid      | . . . | $H + S O_3$                |
| Sulphuric Acid       | . . . | $H + (S O_3 + O)$          |
| Hyposulphurous Acid  | . . . | $H + (S O_3 + S)$          |
| Hyposulphuric Acid   | . . . | $H + (S O_3 + SO_3)$       |
| Trithionic Acid      | . . . | $H + (S O_3 + SO_3 + S)$   |
| Tetrathionic Acid    | . . . | $H + (S O_3 + SO_3 + S_2)$ |
| Pentathionic Acid    | . . . | $H + (S O_3 + SO_3 + S_3)$ |
| Chlorosulphuric Acid | . . . | $H + (S O_3 + Cl)$         |
| Nitrosulphuric Acid  | . . . | $H + (S O_3 + NO_2)$       |

Here we see that the addition to the radical  $SO_3$ , of oxygen, of sulphur, of its own elements  $SO_3$ , of the same with sulphur, of chlorine, or of hyponitrous acid, does not effect the neutralising power, that being dependent on the amount of replaceable hydrogen, which is the same in all.

I have here entered into some detail on the subject of the true constitution of acids, because the acids of sulphur form an admirable illustration of the superior simplicity of the new view of acids and salts, according to which, an acid may be defined as,—A compound of hydrogen with a radical, simple or compound, in which the hydrogen may be replaced by its equivalent of metal: while a salt is,—A combination of a simple or compound radical with a metal; the different salts of one metal corresponding with the oxides of the same metal.

It is obvious that even when a chemical combination or change is represented in a formula according to the old view, as is the case in almost all existing works, we can easily transpose the formula so as to express the new view. Thus, sulphate of potash, on the old view, is  $KO, SO_3$ ; on the new it is  $K, SO_4$ ; or if we express the action of iron on sulphuric acid on the former view, by  $Fe + HO, SO_3 = H + FeO, SO_3$ , it is more simple on the latter,  $Fe + H, SO_4 = H + Fe, SO_4$ .

While, therefore, in order to avoid confusion, I shall generally



use, in equations, the older formula for acids and salts, I shall give the new formula for the principal acids, as I have done for sulphuric and nitric acids, so that the student may, if he please, convert the equations into the new form.

Fremy has described a singular series, or rather several series, of salts containing with potash, sulphurous acid, hyponitrous acid and water. They are formed when sulphurous acid acts on hyponitrite of potash, if a large excess of alkali be present. If we suppose the potash to be present in them as hyponitrite, then the following table represents their composition :—

|                      |   |
|----------------------|---|
| Sulphazite of potash | . 3 (KO, NO <sub>3</sub> ) + 3 SO <sub>2</sub> + 3 HO = 3 KO + S <sub>3</sub> NH <sub>3</sub> O <sub>12</sub>   |
| Sulphazate of do.    | . . 3 (KO, NO <sub>3</sub> ) + 4 SO <sub>2</sub> + 3 HO = 3 KO + S <sub>4</sub> NH <sub>3</sub> O <sub>14</sub> |
| Sulphazotate of do   | . . 3 (KO, NO <sub>3</sub> ) + 5 SO <sub>2</sub> + 3 HO = 3 KO + S <sub>5</sub> NH <sub>3</sub> O <sub>16</sub> |
| Sulphammonate of do. | 4 (KO, NO <sub>3</sub> ) + 8 SO <sub>2</sub> + 3 HO = 4 KO + S <sub>8</sub> NH <sub>3</sub> O <sub>22</sub>     |

These salts are decomposed when their solutions are heated, and even slowly in the cold. The last named salt, the sulphammonate, is formed when solutions of sulphite and hyponitrite of potash are mixed, and is deposited in fine silky needles. Soda appears not to form any corresponding salts.

#### SULPHUR AND HYDROGEN.

##### a. Sulphuretted Hydrogen. HS = 17.

SYN. *Hydrosulphuric Acid*.—This compound is formed when hydrogen and sulphur come in contact in the nascent state. It is best prepared by causing diluted hydrochloric or sulphuric acid to act on sulphuret of iron in the apparatus figured, when sulphuretted hydrogen is disengaged as a gas, which may be collected over warm water, or solution of salt. The action is as follows :  $\text{FeS} + \text{HCl} = \text{FeCl} + \text{HS}$ . It may also be obtained pure by heating tersulphide of antimony with hydrochloric acid, when the following action ensues :  $\text{SbS}_3 + 3 \text{HCl} = \text{SbCl}_3 + 3 \text{HS}$ . The gas should in all cases be purified by passing it through a little water.



Sulphuretted hydrogen is a gas, transparent and colourless, having a very offensive and peculiar smell, which is well known as that of putrid eggs. It is liquefied by a pressure of 17 atmospheres, and the liquefied gas is solidified at  $-122^\circ \text{F.}$ , to a transparent solid. When respired, even although much diluted with air, it is highly deleterious, and as it is often formed where animal matters or excrements putrefy, as in burying-vaults and

cloacæ, it not unfrequently causes the death of workmen who suddenly come in contact with it. It is here formed by the deoxidising action of organic matter on sulphates, which yield sulphurets, and these, decomposing water, give rise to sulphuretted hydrogen. In the same way the sulphuretted hydrogen of mineral springs is formed. The smell of the gas ought, in all confined spaces, to be viewed as a warning of danger. The presence of the gas may also be recognised by its power of blackening the salts of lead, owing to the formation of the black sulphuret of lead.

This gas is combustible, burning with a bluish flame, and producing sulphurous acid gas and water. Its Sp. G. is 1.177. Water absorbs 2 or 3 times its volume of the gas, and acquires its smell and a nausous sweetish taste. By contact with the air, the solution is gradually decomposed: water is formed and sulphur deposited. Sulphuretted hydrogen water must, therefore, be kept in small phials, quite full and closely stopped.

Sulphuretted hydrogen has the properties of a weak acid; it reddens litmus feebly, and acts on bases, forming with them water and metallic sulphurets:  $HS + MO = HO + MS$ . As the sulphurets of some metals are soluble while those of others are insoluble, as moreover the oxides of some of the latter are not decomposed by sulphuretted hydrogen when dissolved in an acid, the action of this gas on solutions of metals in acids affords us a great deal of information, according as a precipitate of sulphuret is formed or not, the colour of the precipitate being also frequently characteristic, as will be described under the individual metals: this renders sulphuretted hydrogen a most useful re-agent in detecting and separating from each other metallic compounds. Where the gas is unable to decompose the metallic salt while yet the sulphuret of the metal is insoluble, a soluble sulphuret, such as that of potassium or ammonium, instantly produces the desired precipitate. Such is the case in solutions of zinc, iron, manganese, cobalt, and nickel; while sulphuretted hydrogen alone precipitates such metals as lead, copper, mercury, silver, bismuth, arsenic, antimony, &c.

Mineral waters exist, as at Harrowgate, which contain sulphuretted hydrogen, easily recognised by its smell and by the property of blackening the salts of lead, silver, and several other metals. The gas in these waters arises from the slow and continued putrefaction of matters containing sulphur, such as albumen, fibrine, &c., or from the deoxidation of sulphates by organic matter, in contact with water. These sulphureous waters are used in medicine, both internally and externally (as baths), with great advantage. In many cases the

artificial sulphuretted hydrogen water, formed by passing the gas through water, previously boiled and allowed to cool, may be substituted for them.

b. Persulphide of Hydrogen.  $\text{HS}_5$  ? or  $\text{HS}_2$  ?

This compound is formed when alkalies, such as potash or lime, are boiled with excess of sulphur, and the solution which is of a deep yellow or orange colour, is poured into a large excess of moderately strong hydrochloric acid, made by mixing equal parts of concentrated acid and water. A heavy, somewhat viscid, transparent, yellowish liquid of Sp. G. 1.769, falls to the bottom, which is the compound in question. The precise nature of all the changes which take place in this process is not known ; but it is probable that a sulphuret of the metal is formed in the first stage, such as persulphide of potassium  $\text{KS}_5$  ; and that a hyposulphite is generated at the same time, possibly according to the formula  $3\text{KO} + \text{S}_{12} = \text{KO}, \text{S}_2\text{O}_2 + 2\text{KS}_5$ . In the second stage, we have probably  $\text{KS}_5 + \text{HCl} = \text{KCl} + \text{HS}_5$ . But as the composition of persulphide of hydrogen is not precisely determined, and as the persulphide appears to dissolve an excess of sulphur, we cannot be certain that this is the true explanation. Thénard considers persulphide of hydrogen  $\text{HS}_2$ , and to be analogous to the peroxide of hydrogen  $\text{HO}_2$ . But his own analysis always gave far more sulphur than corresponds to his formula, and the analogy he pointed out is very obscure and doubtful.

Persulphide of hydrogen soon undergoes spontaneous decomposition, even if kept in sealed tubes, resolving itself into sulphur and sulphuretted hydrogen. In a strong sealed tube, the sulphuretted hydrogen, by its own pressure, is liquefied, and floats above the sulphur, which is deposited in transparent crystals. Persulphide of hydrogen seems to have feeble acid properties. In contact with alkalies, it reproduces water and the metallic persulphuret.  $\text{HS}_5 + \text{KO} = \text{HO} + \text{KS}_5$ .

SULPHUR AND NITROGEN.

Sulphurets of Nitrogen.  $\text{NS}_3 = 62$ ,  $\text{NS}_2 = 46$ .

When chloride of sulphur,  $\text{SCl}_2$ , acts on dry ammonia  $\text{NH}_3$ , a compound is formed,  $\text{SCl}_2, 2\text{NH}_3$ . By the action of water on this there is formed, among other products, a greenish yellow solid body, which is said to be tersulphide of nitrogen  $\text{NS}_3$ . By contact with water, it is gradually converted into hyposulphurous acid and ammonia : for  $2\text{NS}_3 + 6\text{HO} = 2\text{NH}_3 + 3\text{S}_2\text{O}_2$ .—(Soubeiran).

According to Fordos and Gélis, when chloride of sulphur is dissolved in 10 or 12 vols. of bisulphide of carbon, and a current of dry ammonia passed through the solution till the brown colour of the deposit which is formed disappears, the yellow liquid, filtered from the sal-ammoniac, deposits by spontaneous evaporation, golden yellow rhombic crystals, which are said to be bisulphide of nitrogen,  $\text{NS}_2$ . It explodes when heated to  $314^\circ$ , and also on percussion, with great violence. It has a faint smell and irritates the membrane of the nose and eyes painfully. It is insoluble in water, which slowly decomposes it; soluble in bisulphide of carbon; less so in alcohol, ether, and oil of turpentine.

When aqua ammoniæ acts on chloride of sulphur, a variety of products are formed, among which is one, a white crystallisable solid, soluble in alcohol, which appears to consist chiefly of sulphur and nitrogen. Its nature is not yet ascertained, but it is distinguished by the property of dissolving in an alcoholic solution of potash with a deep purple colour, which soon disappears, while ammonia is given off, and crystals of hyposulphite of potash are deposited.—(W. G.)

#### SULPHUR AND AMMONIUM.

a. Protosulphuret of Ammonium.  $\text{NH}_4\text{S} = \text{Am S} = 34$ .

SYN. *Hydrosulphuret of Ammonia*.—This compound is formed when 1 vol. of dry ammoniacal gas is mixed with  $\frac{1}{2}$  vol. of sulphuretted hydrogen,  $\text{NH}_3 + \text{HS} = \text{NH}_4\text{S}$ . It is best obtained by distilling a mixture of chloride of ammonium (sal-ammoniac) and sulphuret of barium, or of calcium.  $\text{BaS} + \text{NH}_4\text{Cl} = \text{BaCl} + \text{NH}_4\text{S}$ . It forms colourless crystals, which are volatile, and dissolves readily in water. The solution becomes yellow by the gradual action of the atmospheric oxygen; it smells of sulphuretted hydrogen and ammonia; and in fact this solution may be more conveniently prepared by taking two equal portions of aqua ammoniæ, and saturating one of them completely with sulphuretted hydrogen. This produces, first, sulphuret of ammonium, and then a compound of that body with sulphuretted hydrogen,  $\text{NH}_4\text{S} + \text{HS}$ . The other half of the aqua ammoniæ is then added, and we have  $(\text{NH}_4\text{S} + \text{HS}) + \text{NH}_3 = 2\text{NH}_4\text{S}$ .

Sulphuret of ammonium, or hydrosulphuret of ammonia, as it is called, is very much used as a test and re-agent in detecting and separating metals. It converts into sulphurets many oxides on which sulphuretted hydrogen does not act, and it also dissolves many metallic sulphurets.

The compound above mentioned, which is formed when

ammonia is completely saturated with sulphuretted hydrogen,  $\text{NH}_4\text{S} + \text{HS}$ , possesses very nearly the same properties, and may be used for the same purposes. It may be called the hydrosulphuret of sulphuret of ammonium.

Both the preceding compounds, when pure, are colourless ; and their solution, mixed with acids, gives off sulphuretted hydrogen, without the deposition of sulphur. By keeping, however, they become yellow, and acids cause a precipitation of sulphur. This is owing to the formation of persulphuret of ammonium, which is accompanied by that of hyposulphite of ammonia.

#### b. Persulphuret of Ammonium.

This compound is formed when either of the preceding is digested with sulphur. There seem to be several sulphurets of ammonium, as of potassium (which see), containing from 2 to 5 eqs. of sulphur. When  $\text{NH}_4\text{S}$  is exposed to the air, we may suppose the ammonium of 1 eq. to be oxidised (as is the case with potassium) and to be converted into free ammonia,  $\text{NH}_4$ ,  $\text{O} = \text{NH}_3$ ,  $\text{HO}$ , while the sulphur of that equivalent unites with the other, forming  $\text{NH}_4\text{S}_2$ . When the compound  $\text{NH}_4\text{S} + \text{HS}$  is exposed to the air, it is the hydrogen of the sulphuretted hydrogen which is oxidised, while its sulphur forms the bisulphuret of ammonium. When sulphur is digested with either of the preceding compounds, different persulphurets of ammonium are probably formed ; and where the sulphur is in excess, it yields, in all probability, the compound  $\text{NH}_4\text{S}_5$ , analogous to persulphuret of potassium,  $\text{KS}_5$ .

All the yellow sulphurets of ammonium have the same useful properties as the protosulphuret in relation to metallic compounds, and some of them dissolve certain metallic sulphurets still more readily. The persulphuret of ammonium or sulphuretted hydrosulphuret of ammonia, as it is sometimes called, is, therefore, very much used in analysis. It is distinguished from the protosulphuret by the action of acids, which cause a precipitate of sulphur, and by its yellow or orange colour. The solution of protosulphuret of ammonium, when kept, becomes gradually yellow, from the formation of persulphuret ; so that, in fact, the latter is always present in the usual forms of this valuable reagent.

Sulphuret of ammonium, under the name of hydrosulphuret of ammonia, is used in medicine. It ought to be given alone, in pure water, as it is decomposed by most acids or salts. The hydrated persulphuret has long been known as Boyle's fuming liquor, which was obtained by distilling 3 parts of slaked lime,

2 of sal-ammoniac, and 1 of sulphur, into a receiver, containing 3 parts of water. Thus prepared, it was an orange-coloured liquid, of oily consistence, fuming in the air, and having a very offensive sulphurous smell. This preparation, however, contains variable proportions of free ammonia. It dissolves much sulphur, and deposits pentasulphuret of ammonium,  $\text{NH}_4\text{S}_5$ , in opaque orange-yellow rhombic prisms.

#### SULPHUR AND CHLORINE.

##### a. Dichloride of sulphur. $\text{S}_2\text{Cl} = 67.5$ .

Formed when chlorine is passed through a vessel containing flowers of sulphur, until nearly the whole sulphur has disappeared. The liquid formed is then purified from excess of chlorine by distillation from flowers of sulphur. It is a yellow, fuming, pungent liquid, boiling at  $280^\circ$ . The Sp. G. of the liquid is 1.687; that of the vapour is 4.70. It is decomposed by water, yielding hydrochloric acid, hyposulphurous acid, and sulphur.

##### b. Protochloride of sulphur. $\text{SCL} = 51.5$ .

When an excess of chlorine is passed through the preceding compound, and the liquid is repeatedly distilled at about  $140^\circ$ , the protochloride is obtained pure. It is a deep reddish-brown liquid, which boils at  $147^\circ$ . Its Sp. G. is 1.625; that of its vapour, 3.68. When acted on by water, it yields hydrochloric acid and hyposulphurous acid, the latter being soon spontaneously decomposed,  $2\text{SCL} + 2\text{HO} = 2\text{HCl} + \text{S}_2\text{O}_2$ .

#### SULPHUR AND BROMINE.

Bromine combines readily with sulphur, and produces compounds analogous to the preceding.

#### SULPHUR AND IODINE.

When 1 part of sulphur and 8 of iodine are mixed and gently heated, they immediately combine and liquefy. On cooling, the liquid, which is dark brown, consolidates into a steel grey crystalline solid, which is the iodide of sulphur. It must be kept in well-closed bottles, as it is destroyed by the access of air, iodine being given off. Its composition is probably  $\text{SI}$ . It is used in medicine as a remedy in various cutaneous diseases.

No compound of sulphur and fluorine is yet known.

#### 9. SELENIUM. $\text{Se} = 39.5$ .

This element occurs in very small quantity, chiefly in certain varieties of pyrites, the sulphur from which, when converted

into sulphuric acid, leaves in the chambers a deposit, consisting of sulphur, selenium, and some metals : and from this the selenium is obtained. Some kinds of fuming sulphuric acid contain a little selenium, which separates on the addition of water as a red powder. Different processes are employed for extracting selenium from the deposit above mentioned ; but the essential parts are, oxidising and dissolving the selenium by means of aqua regia, separating the dissolved metals by sulphuretted hydrogen, &c., and finally deoxidising the selenious acid by means of sulphite of ammonia and hydrochloric acid.

Or the residue of the sulphuric acid chambers at Fahlun is deflagrated with nitre and carbonate of potash, by which means seleniate of potash is formed. This is dissolved, hydrochloric acid added, and the whole evaporated to a small bulk, when the selenic acid is reduced to selenious acid. A current of sulphurous acid now precipitates the selenium as a dark vermilion red powder.

The precipitated selenium appears as a red powder, which, when heated, melts a little above  $212^{\circ}$ , and on cooling forms a brittle mass, nearly black, but transmitting red light in thin plates. Its Sp. G. varies from 4.3 to 4.8. It is then amorphous, with a glassy fracture, but can be obtained also in a crystalline state, in which form it does not melt till  $420^{\circ}$ , when it gives out much heat and becomes amorphous. When more strongly heated it volatilises at a heat below redness, yielding a yellow gas, which condenses into a crystalline dark red powder on a cold surface.

Selenium is extremely analogous to sulphur, except in colour ; and this analogy is still more striking in its combinations. When heated in the air it takes fire, burns with a blue flame, and produces a gaseous compound, oxide of selenium,  $\text{SeO}$ , which has a most penetrating and characteristic odour of putrid horse-radish. By this character selenium is easily recognised in minerals containing it, before the blow-pipe.

#### SELENIUM AND OXYGEN.

These elements combine in three proportions—

a. Oxide of Selenium.  $\text{SeO} = 47.5$ .

This compound has been already mentioned. It is formed when selenium burns, and is gaseous ; it is not acid, and has no analogy with any of the oxides of sulphur.

b. Selenious Acid.  $\text{SeO}_2 = 55.5$ .

This acid is formed when selenium is dissolved in nitric acid,

and the solution evaporated to dryness. It is a solid, which when heated to a point short of redness, is converted into a yellow gas, condensing again into acicular crystals. It is very soluble in water, and has an acid taste. In composition it corresponds to sulphurous acid. This latter acid and its salts deprive selenious acid and its salts of oxygen, causing selenium to be deposited in the uncombined state. It is also deoxidised, and the selenium deposited as red powder, by digesting its solution with iron or zinc. With bases it forms neutral selenites, biselenites, and quadriselenites. Those of the alkalies are soluble; the rest insoluble. When dissolved in water or hydrochloric acid, they are decomposed by sulphurous acid, the selenium appearing as a red powder.

c. Selenic Acid.  $\text{HO, SeO}_3 = \text{H, SeO}_4 = 72.5$ .

This acid is formed when selenium is oxidised by fusion with nitre. The fused mass is dissolved in water, and the selenic acid precipitated as seleniate of lead by adding a salt of lead. The seleniate of lead is decomposed by sulphuretted hydrogen, and the filtered solution of selenic acid cautiously evaporated till it has the Sp. G. 2.625. It is now hydrated selenic acid,  $\text{HO, SeO}_3$ , or rather  $\text{H, SeO}_4$ , and, when heated, is resolved into selenious acid, oxygen, and water. It is very acid and corrosive, and resembles sulphuric acid very much. It may be recognised by the action of hydrochloric acid, which reduces it to selenious acid, chlorine being set free. Selenic acid is not decomposed by sulphurous acid (as selenious acid is), or by sulphuretted hydrogen. It produces intense heat when mixed with water.

With bases, for which it has great affinity, selenic acid forms salts, called seleniates, which are isomorphous with the corresponding sulphates, and entirely resemble them in external characters.

#### SELENIUM AND HYDROGEN.

Seleniuretted Hydrogen.  $\text{HSe} = 40.5$ .

**SYN. Hydroselenic acid.**—This compound is obtained, like sulphuretted hydrogen, which it much resembles, by the action of acids on metallic seleniurets.  $\text{MSe} + \text{HCl} = \text{MCl} + \text{HSe}$ .

It is a colourless gas, of Sp. G. 2.795, which is combustible, and when burned gives off the characteristic odour of oxide of selenium. Seleniuretted hydrogen itself has a smell resembling that of sulphuretted hydrogen, and when respired is even more poisonous than that gas. A small bubble of it produces much and painful irritation of the mucous membrane of the nose and



eyes; and if it reaches the bronchi, excites severe cough, in addition to its poisonous action if absorbed into the blood. The presence of a small quantity of it in sulphuretted hydrogen seems to exalt the poisonous energy of the latter. Like sulphuretted hydrogen, this gas is absorbed by water, and precipitates most metallic solutions, yielding seleniurets corresponding to the respective oxides. Most of these seleniurets are black or dark brown; but those of zinc, manganese, and cerium are flesh red.

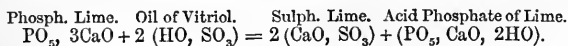
Nothing is known of the compounds of selenium with nitrogen. With ammonia it is probable that seleniuretted hydrogen forms seleniuret of ammonium,  $\text{NH}_4\text{Se}$ , and hydro-seleniuret of seleniuret of ammonium,  $\text{NH}_4\text{Se} + \text{HSe}$ .—(Bineau).

Chloride of selenium appears to be analogous to chloride of sulphur; and the same may be said of the bromide and iodide.

#### 10. PHOSPHORUS. P = 32.

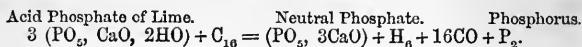
This element occurs abundantly in the bones of animals, in combination with oxygen and metals, as phosphate of lime, phosphate of magnesia, &c. It is also an ingredient, in some unknown form of combination, of vegetable and animal fibrine and albumen, and is constantly present in the urine and excrements. In the mineral kingdom it occurs as phosphate of lime (apatite), phosphate of alumina (wavellite), phosphate of lead, copper, &c.

To obtain phosphorus pure, 10 parts of burnt bones are mixed with 30 or 40 parts of water, and 6 parts of oil of vitriol gradually added. After 24 hours, 50 or 60 parts of water are added to the mixture, and the whole well stirred and digested for a day or two. The strained liquid is evaporated to the consistence of thick syrup, and is then acid phosphate of lime. The first process is thus represented,



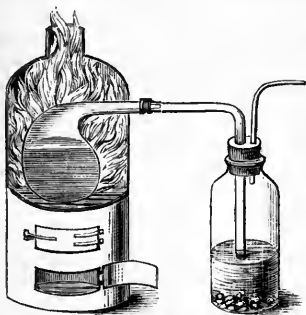
It is now mixed with  $\frac{1}{4}$  of its weight of powdered charcoal, dried and gently ignited. The mass is then gradually heated to whiteness in a stoneware or iron retort, the neck of which ends in a wide bent tube, which dips a little under water.  $1\frac{2}{3}$  of the phosphoric acid in the acid phosphate of lime are deoxidised by the charcoal, and phosphorus is set free, which distils over, and condenses under the water. Owing to the presence of water in the mass, part of the phosphorus is disengaged in combination with hydrogen, forming a spontaneously combustible gas. Care

must therefore be taken to avoid explosions. The essential action is thus represented :



Of course the chief gas disengaged is carbonic oxide, CO.

The phosphorus is now to be melted under water, and squeezed through chamois leather, which separates impurities.



It is lastly melted under water, in funnels with long cylindrical necks, stopped below. Into the necks of the funnels the phosphorus runs, and when cold may be pushed out in the form of solid cylinders.

Pure phosphorus, in the ordinary state, or  $\text{Pa}$ , is a colourless, or very pale yellowish, transparent, or translucent solid, of the consistence

of wax. Its Sp. G. is 1.83. At  $113^\circ$  it melts, and at  $572^\circ$  it boils, distilling completely in close vessels. It has, in the solid form, neither taste nor smell; but it gives off vapours in the air, which, undergoing a slow combustion, cause it to be luminous in the dark. It gives out an odour of garlic; and in solution it has an acrid disagreeable taste. Phosphorus is insoluble in water, soluble in alcohol, ether, oils, sulphuret of carbon, and chloride of phosphorus. From the latter liquids it is often deposited in octohedral and dodecahedral crystals. It is very poisonous, but is used in medicine in very small doses.

When kept in vessels exposed to light, phosphorus becomes yellow, or even brown, externally, owing to some unexplained change. This probably depends on the partial conversion of phosphorus into the red allotropic form of the element,  $\text{P}_3$ , into which it is entirely changed by being kept for a time heated nearly to its boiling point. The red phosphorus is amorphous, has a Sp. G. of 2.14, is unchanged in air at ordinary temperatures, and when heated, does not take fire till it reaches nearly  $500^\circ$ . It is insoluble in bisulphide of carbon, terchloride of phosphorus, or naphtha. When heated still higher, it distils over in the ordinary state.  $\text{Pa}$  must always be kept under water, and never taken into the fingers, for it is so combustible as occasionally to take fire from contact

with the warm hand, where, as it melts and continues to burn, it inflicts frightful injuries.

When heated in air, phosphorus takes fire, and burns with a bright light, producing much white smoke, which is anhydrous phosphoric acid,  $\text{PO}_5$ . Finely divided phosphorus, as already stated, when exposed to air, first undergoes slow combustion, and after a time exhibits spontaneous combustion, bursting into flame. This is, perhaps, due to ozone, which is always formed in air when in contact with phosphorus. When heated in oxygen, it burns with a light so dazzling that the eye cannot endure it. In contact with chlorine, bromine, or iodine, without the aid of heat, combustion takes place spontaneously, while the phosphorus combines with these metalloids.

It appears that there are several other allotropic forms of phosphorus, which are not yet, however, sufficiently well-known. One is formed on the outside of bits of phosphorus kept in water exposed to light; it is white and opaque. Another is obtained by heating pure phosphorus to near its boiling point and suddenly cooling it. This resembles the viscid form of sulphur. A third is formed when melted phosphorus is suddenly cooled, it is black and opaque.

Advantage is taken of the less dangerous character, and less ready inflammability of red phosphorus, in the preparation of many compounds of that element, and in the manufacture of matches.

#### PHOSPHORUS AND OXYGEN.

Phosphorus, in the ordinary state, combines very readily with oxygen. Even at the ordinary temperature it undergoes a slow combustion in air, ozone being first produced, and gives out vapours which are luminous in the dark. It frequently happens that the heat developed by this slow combustion gradually reaches the point at which the phosphorus takes fire; hence the spontaneous combustion of phosphorus, if left exposed to the air, and the necessity of keeping it under water. Many powders, such as powder of platinum, charcoal, lamp-black, &c., when sprinkled on dry phosphorus, cause it to take fire; no doubt because these powders absorb and condense oxygen in their pores, and thus bring it into close contact with the phosphorus.

Many different kinds of instantaneous lights are made with phosphorus, owing to its ready combustibility by friction, especially when chlorate of potash is used.

We are acquainted with four compounds of phosphorus and oxygen.

a. Oxide of Phosphorus.  $P_3O_2 = 120$ .

This oxide is obtained by causing a current of oxygen to come in contact with phosphorus under boiling water. Combustion takes place, and some phosphoric acid is formed; but a part of the phosphorus forms an insoluble cinnabar-red powder, which is oxide of phosphorus,  $P_3O_2$ .

It burns, if heated, nearly to redness, in the air; if heated in close vessels, it is resolved into phosphorus and phosphoric acid,  $5P_3O_2 = 2PO_5 + P_{13}$ . It is oxidised with combustion by nitric acid, and takes fire in chlorine gas.

b. Hypophosphorous Acid.  $PO = 40$ .

In the separate or hydrated state,  $HO$ ,  $PH_2O_3$ , or  $H$ ,  $PH_2O_4$ , the anhydrous acid retaining 2 eqs. water as essential, while a third is basic. This acid is formed when phosphurets of the alkaline metals act on water, or when phosphorus is boiled with alkalis and water, phosphoric acid and phosphuretted hydrogen gas being formed at the same time. The two acids combine with the base; and if this be lime or baryta, the hypophosphite being soluble, is easily separated from the insoluble phosphate. From the hypophosphite of baryta, sulphuric acid removes the baryta, and the hypophosphorous acid is left, dissolved in water. By gentle evaporation it may be obtained as a deliquescent crystalline mass, which is the hydrated acid.

When heated in close vessels, this acid is resolved into phosphuretted hydrogen gas and phosphoric acid. Thus,  $2(PO, 3HO) = PH_3 + PO_5, 3HO$ . It is a powerful deoxidising agent, taking oxygen from many other substances, and passing into phosphoric acid. With bases, it forms salts called hypophosphites, which are all soluble in water, and which, when heated, are dissolved into phosphates and phosphuretted hydrogen.

If to a solution of hypophosphorous acid sulphate of copper be added, and the whole warmed to about  $130^\circ$ , a precipitate is formed, which is said to be a hyduret or hydride of copper,  $Cu_2H$ . If the liquid be heated to the boiling point, this substance is resolved into hydrogen gas and metallic copper. This singular reaction, which is not yet explained, serves to distinguish hypophosphorous from phosphorous acid.

c. Phosphorous Acid.  $PO_3 = 56$ .

In the anhydrous state,  $PO_3$ ; in the separate, or hydrated state (the crystals),  $2HO$ ,  $PHO_4$ , or  $H_2$ ,  $PHO_6$ , the acid retaining 1 eq. of water as essential, and 2 eqs. being basic. It is therefore a bibasic acid.

This acid is formed, along with phosphoric acid, during the slow combustion of phosphorus in air. It is best obtained pure by acting on the terchloride of phosphorus,  $\text{PCl}_3$ , by water.  $\text{PCl}_3 + 6\text{HO} = 3\text{HCl} + \text{PO}_3, 3\text{HO}$ . The hydrochloric acid is easily expelled by a gentle heat, and the aqueous solution of phosphorous acid, if sufficiently evaporated, yields a mass composed of deliquescent crystals. This is the hydrated acid.

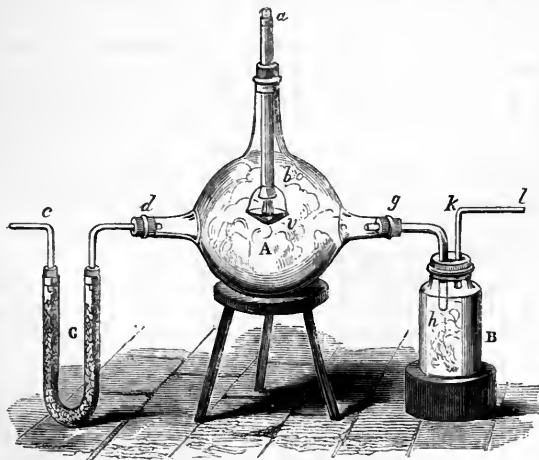
This acid, like the preceding, is a powerful deoxidising agent. When heated in close vessels, the anhydrous acid, obtained by the combustion of phosphorus in rarefied air, yields phosphorus, and anhydrous phosphoric acid,  $5\text{PO}_3 = 3\text{PO}_5 + \text{P}_2$ . The hydrated acid, in the same circumstances, yields hydrated phosphoric acid and phosphuretted hydrogen gas,  $4(\text{PO}_3, 3\text{HO}) = 3(\text{PO}_5, 3\text{HO}) + \text{PH}_3$ .

With bases phosphorous acid forms salts, which are called phosphites; and the general formula of the neutral phosphites is,  $2\text{MO}, \text{PHO}_4$ , or  $\text{M}_2, \text{PHO}_6$ . The acid phosphites are,  $\left. \begin{matrix} \text{HO} \\ \text{MO} \end{matrix} \right\} \text{PHO}$ , or  $\left. \begin{matrix} \text{H} \\ \text{M} \end{matrix} \right\} \text{PHO}_6$ .

#### d. Phosphoric Acid.

##### 1. Anhydrous Phosphoric Acid. $\text{PO}_5 = 72$ .

This compound is formed only when phosphorus is burned in dry air or oxygen gas, in an apparatus like that figured, the



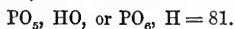
phosphorus being introduced occasionally through the upper tube, and the dry air or oxygen by the bent tube. The current

of gas carries the greater part of the acid into the bottle to the right. It then appears as a white solid, like snow, which, when dropped into water, hisses like red-hot iron, and rapidly dissolves. It also rapidly attracts moisture from the air, and passes into metaphosphoric acid,  $\text{PO}_5$ ,  $\text{HO}$ , or  $\text{PO}_6$ ,  $\text{H}$ ; and this, again, soon changes, in contact with water, especially if heated, into common or hydrated phosphoric acid,  $\text{PO}_5$ ,  $3\text{HO}$ , or  $\text{PO}_8$ ,  $\text{H}_3$ . The anhydrous phosphoric acid, like the anhydrous sulphuric acid, can hardly be said to be an acid body, as it does not exhibit acid properties until it has been brought into contact with water. It has a most intense attraction for water, and is much used to deprive other substances of it, having the great advantage that it does not char organic compounds as sulphuric acid does.

## 2. Hydrated Phosphoric Acid.

There are three different acids to which this name may be given. If we view them as compounds containing water, then they all contain anhydrous phosphoric acid, combined in each with a different proportion of water, and their formulæ will be  $\text{PO}_5$ ,  $\text{HO}$ ;  $\text{PO}_5$ ,  $2\text{HO}$ ; and  $\text{PO}_5$ ,  $3\text{HO}$ . If, on the other hand, we view them as hydrogen acids, then they contain no anhydrous phosphoric acid, but are quite distinct compounds, and their formulæ will be as follows:  $\text{PO}_6$ ,  $\text{H}$ ;  $\text{PO}_7$ ,  $\text{H}_2$ ; and  $\text{PO}_8$ ,  $\text{H}_3$ . The latter view is much more probable, and agrees better with the properties and composition of these acids, and of their salts. The first is called metaphosphoric acid, the second pyrophosphoric acid, and the third common phosphoric acid; or they may be still better designated as monobasic, bibasic, and tribasic phosphoric acids.

### METAPHOSPHORIC, OR MONOBASIC PHOSPHORIC ACID.



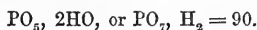
This acid is easily obtained by dissolving phosphorus in diluted nitric acid with the aid of heat, evaporating to a syrup, and exposing the residue to a red-heat, in a platinum crucible. Or the solution of the anhydrous acid may be treated in the same manner; or phosphate of ammonia may be ignited in a platinum crucible. When phosphoric acid has once come in contact with water, it can never be rendered anhydrous by heat; it can only be reduced to the state of monobasic acid.

As thus obtained, it appears in the shape of a colourless and transparent glass, which slowly dissolves in water. It is hence called glacial phosphoric acid. Its solution causes in solutions of silver a white granular precipitate of monobasic phosphate of

silver ; it also coagulates albumen. But if long kept, or if very rapidly boiled, this solution passes into one of tribasic phosphoric acid, and no longer precipitates silver or coagulates albumen. Here 2 eqs. of water enter into the composition of the acid ;  $\text{PO}_5, \text{HO} + 2\text{HO} = \text{PO}_5, 3\text{HO}$ .

With bases, this acid forms one series of salts the monobasic phosphates, the general formula of which is  $\text{PO}_5, \text{MO}$ , or  $\text{PO}_6, \text{M}$ . In these, the hydrogen of the acid is replaced by its equivalent of metal. The precipitate caused by the acid in solutions of silver is one of these salts,  $\text{PO}_5, \text{AgO}$ .

#### PYROPHOSPHORIC, OR BIBASIC PHOSPHORIC ACID.

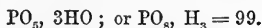


When common or tribasic phosphoric acid,  $\text{PO}_5, 3\text{HO}$ , is heated for some time to  $417^\circ$ , it loses one third of the water it contains, and becomes bibasic, or pyrophosphoric acid. It appears as a viscid syrup, very acid and very soluble in water. Its solution neither precipitates silver nor coagulates albumen ; but if previously neutralised by ammonia it causes in salts of silver a flaky white precipitate of bibasic phosphate of silver,  $\text{PO}_5, 2\text{AgO}$ . The solution of this acid, like that of the preceding soon passes into tribasic acid, especially if heated.

With bases it forms two series of salts, one containing 2 eqs. of base, the other 1 eq. of base, and 1 of water. The former are neutral, and have the general formula  $\text{PO}_5, 2\text{MO}$  ; the latter are acid, and their formula is  $\text{PO}_5, \text{MO}, \text{HO}$ . This acid is much more easily obtained in combination with a base than in the free state, and in fact it was discovered in the salt obtained by igniting the common phosphate of soda, when there is left pyrophosphate or bibasic phosphate of soda,  $\text{PO}_5, 2\text{NaO}$ . The acid salt may be obtained by heating to  $300^\circ$  the monohydrated metaphosphate of soda,  $\text{PO}_5, \text{NaO} + \text{aq.}$  ; when the 1 eq. of water becomes basic, and the result is the formation of the acid pyrophosphate of soda,  $\text{PO}_5, \text{NaO}, \text{HO}$ .

When a pyrophosphate is melted with excess of base, it is converted into a tribasic phosphate. Thus, if pyrophosphate of soda be fused with an additional equivalent of soda, the tribasic salt  $\text{PO}_5, 3\text{NaO}$  is formed, which no longer contains pyrophosphoric acid.

#### COMMON, OR TRIBASIC PHOSPHORIC ACID.



When a solution of any of the preceding acids is evaporated by a moderate heat to the consistence of syrup, the residue is

found to be the tribasic acid  $\text{PO}_3, 3\text{HO}$ . Heated for a long time to  $417^\circ$ , it loses 1 eq. water and becomes bibasic; heated to redness it gives off 2 eqs. water, and becomes monobasic. A diluted solution of either of these gradually becomes tribasic, and this change is very rapidly effected by boiling. Solution of common phosphoric acid neither precipitates silver nor coagulates albumen; but if neutralised by ammonia it causes in salts of silver a pale yellow precipitate of tribasic phosphate of silver,  $\text{PO}_3, 3\text{AgO}$ .

The most economical method of preparing phosphoric acid is to add to the syrupy superphosphate, or acid phosphate of lime, previously described, oil of vitriol, as long as it causes a precipitation of sulphate of lime. The mixture becomes quite thick, and is to be diluted with water, filtered, again concentrated to a syrup, and again tested by adding a few drops of oil of vitriol. When no more sulphate of lime is formed, the solution is free from lime, but still contains phosphate of magnesia and soda. It is to be evaporated and gradually heated to redness in a platinum vessel, by which means all the excess of sulphuric acid is expelled, and a glass is left. To separate the magnesia and soda, this glass is to be dissolved in warm water, and the solution evaporated in a platinum dish, till its temperature reaches  $600^\circ \text{F}$ . and phosphoric acid begins to be expelled along with the water. At this point the thick viscid mass becomes turbid, from the separation of insoluble phosphate of magnesia and soda; and if the same temperature is kept up for a quarter or half an hour, the whole of the magnesia assumes the insoluble form. Water being now added, the pure phosphoric acid dissolves, the insoluble phosphate of magnesia and soda, the latter base probably derived from common salt in the bones, is separated by filtration, and the filtered liquid is a pure solution of phosphoric acid. It is now evaporated and once more gently ignited in a covered platinum vessel. Pure monobasic phosphoric acid is left. It is now dissolved in hot water, and becomes tribasic acid, the form usually employed, as it is the most permanent. Like the other phosphoric acids, it is very acid, but not corrosive. It is occasionally used in medicine.

With bases, common phosphoric acid forms three series of salts, in which the three equivalents of water in the acid are wholly or partially replaced by metallic oxides. Thus, with soda, it forms three salts; 1st, neutral phosphate,  $\text{PO}_3, 3\text{NaO}$ ; 2nd, common phosphate of soda,  $\text{PO}_3, 2\text{NaO}, \text{HO}$ ; 3rd, acid phosphate of soda,  $\text{PO}_3, \text{NaO}, 2\text{HO}$ . In each of these salts there are 3 eqs. of base, but these may be either all soda, or partly



soda and partly basic water. All three salts give with the salts of silver the same yellow precipitate,  $\text{PO}_5, 3\text{AgO}$ ; but the supernatant liquid is only neutral when the neutral phosphate is used; it is acid in the case of the other two salts, because, for every eq. of oxide of silver in the precipitate, 1 eq. of nitric acid has to be neutralised, and this cannot be effected by the basic water, but only by the soda.

When the second or common phosphate of soda is ignited, its basic water is driven off, and bibasic phosphate of soda,  $\text{PO}_5, 2\text{NaO}$ , is left. This salt, dissolved in water, gives with salts of silver a white flaky precipitate of bibasic phosphate, while the supernatant liquid remains neutral.

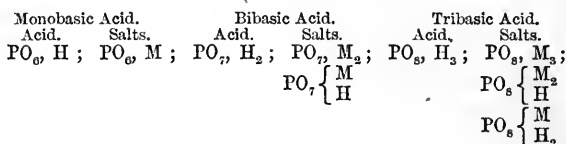
If the third or acid phosphate of soda be ignited, it loses 2 eqs. of basic water, and monobasic phosphate is left, which, if dissolved in water, gives with silver a granular white precipitate of monobasic phosphate, the supernatant liquid remaining neutral.

From the above brief description of the three modifications of phosphoric acid, it will be seen that their characters are distinct and well marked. Graham views them according to the formulæ which assume the presence of water, as three different hydrates of the same anhydrous acid; and he considers that when the anhydrous acid has combined with one, two, or three atoms of water, it acquires and retains, in each case, the power or tendency to combine with one, two, or three equivalents of fixed base. The facility with which one form passes into the other is in favour of this view; it must be observed that it affords no explanation of the remarkable tendency alluded to, but only states the fact, and still leaves unanswered the question, Why does anhydrous phosphoric acid at one time unite with 1 eq., at another with 2 eqs. or 3 eqs. of water? or why does it, by doing so, acquire the tendency to unite with 1, 2, or 3 eqs. of base? We have already seen that anhydrous sulphuric acid forms three hydrates, with 1, 2, and 3 eqs. of water respectively. But there is no tendency in the two latter of these to combine with more eqs. of base than the first. They all yield the same sulphates. What then is the reason, on Graham's hypothesis, why the hydrates of phosphoric acid should act differently?

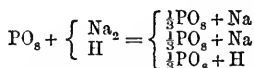
Liebig, on the other hand, considers the three acids as radically different, being formed of hydrogen, united in each to a different compound radical; and that as in the first there is only 1 eq., in the second 2 eqs. and in the third 3 eqs. of hydrogen, the salts must necessarily contain equivalent proportions of metals which, in the two latter, may replace the hydrogen either wholly or partially, as in other polybasic

acids. The formulæ for the acids, on this view, have been given above.

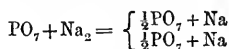
The now-admitted existence of numerous polybasic acids, and the growing tendency to consider all hydrated acids as hydrogen acids, tend to induce us to prefer the latter view, which moreover has the advantage of at least offering an explanation of the different neutralising power of the three acids, which is referred to the amount of replaceable hydrogen they contain. Thus we have—



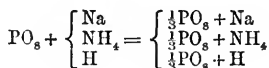
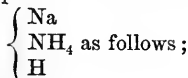
If we begin from the tribasic acid, and represent one of its salts, the common phosphate of soda,  $\text{P}_2\text{O}_8, \left\{ \begin{smallmatrix} \text{Na}_2, \text{ as follows;} \\ \text{H}, \end{smallmatrix} \right.$



We see that when this salt is ignited, 1 eq. of hydrogen is expelled, along with 1 eq. of oxygen, and the 2 eqs. of sodium now neutralise the whole of the remaining phosphorus and oxygen, which is  $\frac{3}{3}\text{PO}_8 - \text{O} = \text{PO}_7$ , and the bibasic salt,  $\text{PO}_7, \text{Na}_2$  results. If this be expressed by



We see that something has been added to the radical previously united with each eq. of sodium without altering its neutralising power. In like manner, if we represent microcosmic salt  $\text{PO}_8,$



We see that when it is ignited, the hydrogen and the ammonium are both expelled, each combined with 1 eq. of oxygen; but as the rest of the phosphorus and oxygen formerly combined with them is not expelled, it enters into the composition of the radical still united with the 1 eq. of sodium, but without affecting its neutralising power. This radical, therefore, becomes

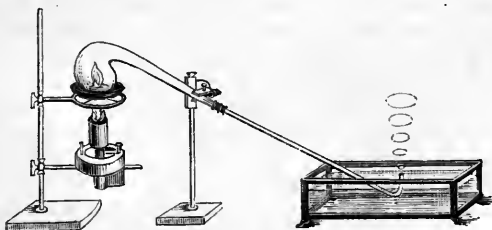
$\frac{3}{2} \text{PO}_3 - \text{O}_2' = \text{PO}_6$ ; and its salt with sodium is  $\text{PO}_6, \text{Na}$ , the monobasic phosphate of soda. If, now, we turn to what was said above of the acids of sulphur, viewed as hydrogen acids, we shall there see many analogous cases of the addition to the acid radical of different quantities of its elements, while the neutralising power remains unchanged. Thus, hydrated sulphurous acid,  $\text{H} + \text{SO}_3$ , by the addition of  $\text{SO}_3 + \text{S}_2$  to its radical becomes tetrathionic acid,  $\text{H}, \text{S}_4\text{O}_6$ , without change of neutralising power. In the phosphoric acids, the neutralising power varies, because the hydrogen varies; but when they are represented, as has been done above, in such a way as to keep the hydrogen (or metal) the same in all, the analogy between them and the acids of sulphur, in regard to the non-dependence of the neutralising power on the nature and proportions of the ingredients of the radical, becomes manifest.

The above is the view which Liebig takes of the nature and formation of the three phosphoric acids. It must be admitted, that it has the advantage of simplicity; that it explains, in a consistent manner, all the known facts; and that it is at present better supported, and rests on fewer assumptions, than any other theory of the constitution either of these acids, or of acids in general.

#### PHOSPHORUS AND HYDROGEN.

Phosphuretted Hydrogen.  $\text{PH}_3 = 35$ .

This compound may be formed by the action of phosphurets of alkaline metals on water, or by the action of phosphorus on boiling alkaline solutions. Thus, phosphuret of calcium, thrown into water, disengages the gas in question; and it is also produced in large quantity by applying heat to a mixture of lime,



water, and fragments of phosphorus, in a retort nearly filled with the mixture, or by boiling phosphorus with an alcoholic solution of potash. The two former methods yield it in a form in which it is spontaneously combustibile on coming in contact

with air or oxygen ; the latter in a form in which it requires the contact of flame in order to burn. The gas in both cases is essentially the same ; but in the former it contains a minute proportion of a compound, not yet isolated, which is spontaneously inflammable, and which, inflaming by contact of air, kindles the gas. This compound is supposed to be  $P_2H_2$ . When the spontaneously inflammable gas is long kept, it deposits a solid compound,  $P_2H$ , and is then no longer spontaneously combustible. Possibly  $2P_2H_2$  yield  $P_2H$  and  $P_2H_3$ .

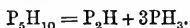
The gas, whether spontaneously inflammable or not, is colourless, and has a very offensive smell of putrid fish. When it burns it produces anhydrous phosphoric acid and water, forming thick white vapours ; and when bubbles of the spontaneously inflammable gas take fire in still air, they form beautiful circular wreaths of vapour, which ascend, gradually widening, till they are dissipated in the air.

The addition of ether, oil of turpentine, and many other substances, destroys the spontaneous inflammability ; but this property may be restored by adding to the gas a minute proportion of nitrous acid.—(Graham.)

Phosphuretted hydrogen is neither acid nor alkaline to test paper ; but it seems to have alkaline tendencies, since it combines with hydriodic acid, forming a neutral crystalline compound, isomorphous with hydriodate of ammonia. It also combines with several metallic chlorides, forming compounds analogous to those produced by ammonia with the same chlorides. Rose, who has described these compounds, points out a considerable analogy between phosphuretted hydrogen and ammonia. This analogy is further shown by the fact that the hydrogen may be replaced by ethyle, methyle, &c., yielding volatile bases, like ethylamine.

It has already been mentioned, that when hypophosphorous and phosphorous acids are heated, they are resolved into phosphoric acid and phosphuretted hydrogen. This gas is consequently given off frequently towards the end of the evaporation of a solution of phosphorus in diluted nitric acid, which at first forms phosphorous acid, by the decomposition of which the gas is produced, causing a sudden combustion at the surface of the evaporating liquid.

Since the above account was printed, M. P. Thénard has published an elaborate Memoir on phosphuretted hydrogen, from which it appears that there exist. 1st, a fluid compound  $PH_2$  or  $5PH_2 = P_5H_{10}$  ; 2nd, a solid compound  $P_2H$  ; and 3rd, the gas  $PH_3$ . The fluid is first formed, and is then spontaneously or very easily resolved into the other two. Thus—



The gas,  $\text{PH}_3$ , acquires its spontaneous combustibility by dissolving some of the liquid  $\text{P}_3\text{H}_{10}$ . In fact this liquid communicates the same property to other gases.

## PHOSPHORUS AND NITROGEN.

Phosphuret of Nitrogen.  $\text{NP} = 46$ .

This is a white insoluble powder, formed by the action of ammonia on terchloride of phosphorus.  $\text{NH}_3 + \text{PCl}_3 = 3 \text{HCl} + \text{NP}$ . It is infusible and fixed in the fire in closed vessels. According to Gerhardts it contains hydrogen.

## PHOSPHORUS AND CHLORINE.

Phosphorus takes fire spontaneously in chlorine gas, forming two compounds.

a. Terchloride of Phosphorus.  $\text{PCl}_3 = 133.5$ .

When phosphorus is made to pass, in the form of vapour, through a tube filled with coarse powder of bichloride of mercury,  $\text{HgCl}_2$ , or when chlorine is slowly passed through a tube or retort containing phosphorus, a volatile colourless liquid is obtained, which is terchloride of phosphorus. It has a Sp. G. of 1.616, and boils at  $173.5^\circ$ .  $3 \text{HgCl}_2 + \text{P}_2 = 3 \text{HgCl} + \text{P}_2\text{Cl}_3$ . Here protochloride of mercury is left, while the excess of chlorine combines with the phosphorus. The terchloride is a pungent fuming liquid, which, in contact with water, yields hydrochloric and phosphorous acids:  $\text{PCl}_3 + 3 \text{HO} = 3 \text{HCl} + \text{PO}_3$ .

b. Pentachloride of Phosphorus.  $\text{PCl}_5 = 209.5$ .

This compound is best formed by passing a current of chlorine through the preceding to saturation. It is a white volatile solid, of pungent smell. In contact with water, it yields hydrochloric and phosphoric acids:  $\text{PCl}_5 + 5 \text{HO} = 5 \text{HCl} + \text{PO}_5$ . When slowly acted on by the vapour of water, pentachloride of phosphorus yields hydrochloric acid and oxychloride of phosphorus,  $\text{PCl}_3\text{O}_2$ . With sulphuretted hydrogen the pentachloride forms a corresponding sulphochloride,  $\text{PCl}_3\text{S}_2$ . This sulphochloride of phosphorus, heated with caustic soda, yields a salt of constitution analogous to that of common phosphate of soda (tribasic, with 2 eqs. of soda), in which the acid is sulphonyphosphoric acid,  $\text{PO}_3\text{S}_2$ . The formula of this salt is  $\text{PO}_3\text{S}_2, 2 \text{NaO}, \text{HO} + 24 \text{ aq}$ . It forms six-sided tables.

## PHOSPHORUS AND BROMINE.—PHOSPHORUS AND IODINE.

With bromine, phosphorus also unites with spontaneous combustion, and forms with it two compounds, said to be analogous to those with chlorine. They are volatile solids of a yellow colour. They decompose water like the chloride, with the production of hydrobromic acid on the one hand, and phosphorous or phosphoric acids on the other.

With iodine, phosphorus combines with great energy, producing much heat, and setting fire to a portion of the phosphorus, unless the elements be brought in contact in a vessel full of carbonic acid. The compound formed first appears as a dark brown liquid, melted by the heat, which solidifies on cooling, and decomposes water with rapidity, giving off hydriodic acid in large quantities. It has been found, that two definite iodides of phosphorus exist, namely, a biniodide,  $PI_2$ , and a teriodide,  $PI_3$ . They are obtained in a state of purity by dissolving the two elements, in due proportion, in bisulphide of carbon. By cooling or evaporation they separate; the biniodide in orange-coloured flexible prisms, which melt at  $230^\circ$ ; the teriodide in dark red six-sided plates, which melt at about  $130^\circ$ , and on cooling form fine prisms.

When 1 eq. of iodine is heated with about 100 eqs. of phosphorus, nearly the whole of the phosphorus is converted into the red variety,  $P\beta$ . There is some risk of explosion in this experiment, in which, according to Brodie, biniodide of phosphorus is formed, and then converted into an allotropic state.

## PHOSPHORUS AND SULPHUR.

When phosphorus and sulphur are heated together under water they combine, often with incandescence, forming several compounds, which are exceedingly inflammable, and having a tendency to explode violently when heated, from some unknown cause, are very dangerous to experiment with. Berzelius has lately examined these compounds, and has described the following. 1.  $P_2S$ . This compound occurs in two states, as a colourless liquid, and as a red powder; 2.  $PS$ . A pale yellow liquid, also as an orange powder; 3.  $PS_{12}$ . Yellow crystals; 4.  $P_3S_2 = P_2S + PS$ . A scarlet powder, changed by distillation into a liquid; 5.  $P_2S_3$ . A yellow fusible solid; 6.  $PS_3$ . A yellow crystallisable solid. It is very remarkable, that several of these compounds occur in two distinct states; and Berzelius conceives that this is owing to the circumstance that, like sulphur, phos-

phorus itself exists in two mechanically distinct states, and that the difference of the two states of the compounds depends on the one containing phosphorus, or sulphur, or both, in its ordinary condition, while in the other the phosphorus, or sulphur, or both, are in the allotropic state, as it is now called.

#### 11. CARBON. $C = 6$ .

This element occurs very abundantly in nature, generally combined. In the pure state, and crystallised, it constitutes the diamond. In a compact form, composed of shining crystalline scales, of a form different from the diamond, and black, it occurs as plumbago or graphite; and in a much less pure form as anthracite coal. It is an essential ingredient of all organised tissues and products, animal and vegetable; and it is also found in the mineral kingdom as the chief component of pit coal and wood coal, which are evidently derived from vegetables; and, further, as carburetted hydrogen gas, the fire-damp, and carbonic acid gas, the choke-damp of coal mines, which are products of the decay of vegetable matter. Carbonic acid is abundant in volcanic districts and in mineral waters, and, combined with lime or magnesia, constitutes extensive rock formations. Carbonate of lime occurs, for example, as marble, limestone, and chalk; and along with carbonate of magnesia as dolomite. When crystallised, it forms calcareous spar. Carbonate of magnesia also forms rocks in some parts of the world. In smaller quantity, the carbonates of baryta, strontia, lead, and some other bases, are also found. Carbonic acid gas is always present in the atmosphere, of which it forms less than  $\frac{1}{1000}$  by weight.

Carbon is artificially prepared by heating organic matter in close vessels as long as any volatile substances are given off. These volatile bodies are compounds of carbon, hydrogen, nitrogen, and oxygen, in various proportions, and the residue is the excess of carbon, which is fixed in the fire, provided oxygen be excluded. Wood thus treated yields common charcoal, which is carbon + the ashes or mineral elements of the wood. Coal yields coke, which is more dense in its structure. Animal matters yield animal charcoal, which contains phosphates, and also nitrogen, probably as paracyanogen. The charcoal from bones is called bone or ivory black, and is of course loaded with phosphate of lime. When oils or resins, which are always rich in carbon, are burned with a deficient supply of oxygen, they yield a great deal of soot, which is called lamp-black. When ignited in close vessels, to expel any traces of oil or volatile matters, this is almost pure carbon.

The diamond, or crystallised carbon,  $C_\alpha$ , is the hardest body known. Its Sp. G. is 3.3 to 3.5. It is also quite infusible, but is easily burned when heated in oxygen, or even in air, and is converted into carbonic acid. It is remarkable for its transparency and high refractive and dispersive power: it is a non-conductor of electricity. In the other (allotropic) form of graphite,  $C_\beta$ , it is black, and crystallised in a different form, which is that of six-sided plates, belonging to the rhomboidal system. Its Sp. G. is from 1.8 to 2.09; and in that of anthracite, or in that of lamp-black and of wood charcoal,  $C_\gamma$ , carbon is amorphous, opaque, black, combustible in air or oxygen. It is, both as graphite,  $C_\beta$ , and charcoal,  $C_\gamma$ , a conductor of electricity. Its Sp. G. is 2. In all its forms, carbon is devoid of taste or smell, insoluble, as such, in all menstrua (although it may be oxidised and dissolved as carbonic acid by strong nitric acid, or aqua regia, with the aid of heat), and altogether fixed in the fire in close vessels.

In open vessels, some varieties of carbon, when heated, take fire, and, if pure, burn entirely away, being converted into carbonic acid gas. Indeed, the attraction of carbon for oxygen at a red-heat exceeds that of almost all other bodies. It is to this property, and to the heat and light, given out in its combustion, that are owing the uses of carbon, as the chief ingredient of all kinds of fuel, whether burned for heat or for light. The same property renders it invaluable as a means of deoxidising metallic oxides, and thus procuring the metals. Carbon possesses also a remarkable power, especially in the more porous forms, of absorbing gases and noxious effluvia, and is much used for purifying air and water. It is also extensively employed to remove colouring matters, for which it has a great attraction, from organic solutions, as in the refining of sugar, and many other processes.

#### CARBON AND OXYGEN.

With oxygen, carbon forms two well-marked gaseous compounds, which shall be here described. The same elements, in other proportions, constitute, according to the opinion which regards oxygen acids as hydrates, certain anhydrous acids, to be described under the head of organic chemistry. As these anhydrous acids, however, are not known in the separate form, we may rather consider the acids in question (the oxalic, mellitic, croconic, and rhodizonic acids) as compounds of hydrogen.

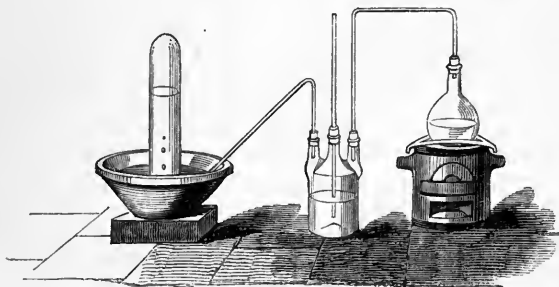
##### a. Carbonic Oxide. $CO = 14$ .

This gas is formed either when carbon is burned with a limited



supply of air, as when air is passed through a mass of red-hot charcoal; or when carbonic acid is brought into contact with red-hot charcoal. In the latter case, the carbonic acid,  $\text{CO}_2$ , is deoxidised, while the carbon is oxidised,  $\text{CO}_2 + \text{C} = 2 \text{CO}$ .

It is best obtained by heating in a retort 1 part of finely-powdered ferrocyanide of potassium (prussiate of potash) along with 10 parts of oil of vitriol. The salt contains cyanide of potassium,  $\text{K}$ ,  $\text{C}_2\text{N}$ , and cyanide of iron,  $\text{Fe}$ ,  $\text{C}_2\text{N}$ . One or both of these salts acts on the sulphuric acid and water yielding sulphate of potash (or of iron), sulphate of ammonia, and carbonic oxide,  $\text{K. C}_2\text{N} + 2 (\text{HO, SO}_3) + 2 \text{HO} = (\text{KO, SO}_3) + (\text{NH}_4 \text{O, SO}_3) + 2 \text{CO}$ . The gas may also be obtained by heating a mixture of a formiate,  $\text{MO, C}_2\text{HO}_3$ , with an excess of oil of vitriol,  $\text{MO, C}_2\text{HO}_3 + \text{HO, SO}_3 = \text{MO, SO}_3 + 2 \text{HO} + 2 \text{CO}$ . When oxalic acid,  $2 \text{HO, C}_4\text{O}_6$ , or an oxalate,  $2 \text{MO, C}_4\text{O}_6$ , is heated with an excess of oil of vitriol, there is obtained a mixture of carbonic oxide and carbonic acid gases;  $2 \text{MO, C}_4\text{O}_6 + 2 (\text{HO, SO}_3) = 2 (\text{MO, SO}_3) + 2 \text{HO} + 2 \text{CO}_2 + 2 \text{CO}$ . By passing the mixed gases through milk of lime, or solution of potash, as in the figure, the carbonic acid is arrested, and the carbonic oxide gas obtained pure.



Carbonic oxide gas may be collected and kept over water. It is transparent and colourless, has neither taste nor smell, and when respired is fatal to animal life. It takes fire when heated to redness in contact with air, as by the approach of a candle, and burns with a lambent clear blue flame, combining with a second equivalent of oxygen, and yielding carbonic acid. Its Sp. G. is 0.9722. The blue flame that is often seen to play on the surface of a large red-hot coal fire is owing to the formation of this gas; the carbonic acid formed at the lower part of the fire being forced to pass through a thick mass of red-hot coal. The formation of this poisonous gas is also one cause of the

danger of slowly burning charcoal in chauffers, in rooms where there is no chimney and little ventilation.

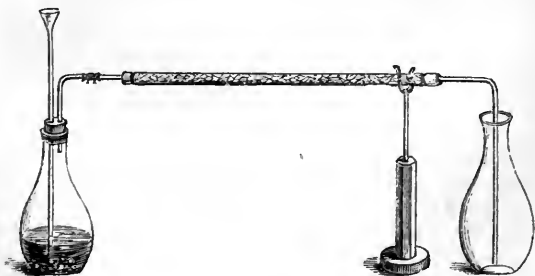
Carbonic oxide is a compound radical ; that is, it acts like an element, combining with elements. Thus it combines with chlorine, with oxygen, with metals. In this point of view it is a most interesting compound ; but, like cyanogen, comes to be treated of as a compound radical in the organic division of this work.

b. Carbonic Acid.  $\text{CO}_2 = 22$ .

SYN. *Fixed Air*.—This gas occurs in a variety of circumstances, which have been noticed above, in treating of carbon. In addition to these, it may here be mentioned that it is formed during the respiration of animals, and that it is a chief product of the vinous or alcoholic fermentation. It is also formed in large quantity in all ordinary combustions, from the oxidation of the carbon in the fuel.

It is best prepared artificially by the action of diluted hydrochloric or sulphuric acid on marble or chalk, which, as already stated, is carbonate of lime,  $\text{CaO}$ ,  $\text{CO}_2$ . Thus we have  $\text{CaO}$ ,  $\text{CO}_2$ ,  $+\text{HCl} = \text{CaCl} + \text{HO} + \text{CO}_2$ . It may be collected, with some loss, over water, which absorbs it to a considerable extent.

It is a transparent and colourless gas, with a rather pungent, subacid smell, and a slightly acidulous taste. Its Sp. G. is 1.527 ; and it is so much heavier than air, that it may be collected in vessels by displacement, as represented in the cut, especially if it be wanted dry, after passing through a tube filled



with chloride of calcium. Lime water is rendered turbid by this gas, the insoluble carbonate of lime being formed ; and by this character it is distinguished from all other gases. It extinguishes flame, and is most deleterious when inhaled. As it is apt, from its great density, to accumulate in the lower part of

wells, pits, or mines, where it is evolved, it is often the cause of fatal accidents. No such place should be entered until a light has been introduced, and found to burn brightly ; if it burns dimly, or is extinguished, the air will certainly destroy life, if respired.

Carbonic acid gas, by a pressure of 36 atmospheres, is liquefied. This is best accomplished by condensing the gas, by means of a pump, into a strong copper vessel, such as is used for air-guns. The liquid carbonic acid, by its almost instantaneous evaporation, when allowed to escape through a jet, produces so much cold as to freeze a part of the gas into a white solid like snow. The solid carbonic acid evaporates slowly, but, if mixed with ether, more rapidly, so as to freeze mercury easily. The liquid acid expands by heat in a greater degree than even the gas does.

Carbonic acid gas is absorbed by water, particularly under increased pressure, and gives to that liquid an acidulous taste and the power of reddening litmus ; although on exposure to the air, or on boiling, the gas is given off, and the blue colour is restored. With the bases, it unites, forming salts, which are called carbonates ; but in the soluble carbonates the alkali is not neutralised, and many carbonates of the bases, especially of ammonia, may be obtained, in all of which the properties of the alkali predominate. It would appear, from this, that carbonic acid is not a true acid, although it combines with bases. We shall hereafter see that one or two other oxygen acids which, like it, do not form hydrates, are, in like manner, destitute of the true character of acids.

The sparkling and effervescing properties of many kinds of wine, of beer, and of soda water, are owing to the presence of carbonic acid. The mineral waters, in which it occurs free, are known by their sparkling, and are much used.

The importance of carbonic acid in the economy of nature is very great. It forms the chief food of plants, and the source of their carbon, and as fast as it is consumed by them it is restored to the air by the respiration of animals, by combustion and by decay, so that its amount in the air never varies much, and always suffices for vegetation.

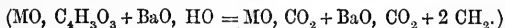
Oxalic acid, as well as croconic, rhodizonic, and mellitic acids, have been by some considered compounds of carbon with oxygen ; but they all contain hydrogen as an essential element, and belong, more properly, to organic chemistry. Oxalic acid, for example, is  $C_4H_2O_8 = C_4O_6, 2HO$ . These acids will be described in the organic part of this work.

## CARBON AND HYDROGEN.

These two elements combine together in a vast number of proportions, and being both combustible, give rise to compounds, all of which are highly inflammable, and which resemble each other in chemical characters generally. They are often called carbo-hydrogens. At the ordinary temperature, some are solid, as paraffine and naphthaline; many are liquid, as oils of turpentine and lemons, naphtha, &c.; and some are gaseous, namely, light carburetted hydrogen gas, and olefiant gas. All of these compounds are either vegetable products, or arise from the decay or the destructive distillation of organic matter. As, however, the two gases just named mixed in various proportions with air, constitute the fire-damp of coal-mines, and consequently occur in the mineral kingdom, and as each of them is the type of a series, we shall describe them here, leaving the remainder for organic chemistry.

a. Light Carburetted Hydrogen.  $C_2H_4 = 16$ .

**SYN. Marsh Gas.** This gas forms the chief part of the combustible gases, which, issuing from the seams in the coal, mixes with the air of the mines, and produces the explosive fire-damp. It is produced nearly pure, when vegetable matter decays under stagnant water. The bubbles which rise are found to consist of this gas, with a little carbonic acid, which may be removed by solution of potash. The gas may also be formed artificially by heating an acetate,  $MO, C H_3 O_3$ , with an excess of hydrate of baryta. We have then



The gas is colourless and inflammable, burning with a yellowish flame, and forming carbonic acid and water with the oxygen of the air.  $CH_2 + O_4 = CO_2 + 2 HO$ . Its Sp. G. is 0.5555. When mixed with twice its volume of oxygen and set fire to, it explodes violently. The same result follows, but with less violence, when it is mixed with 10 vols. of air, which contains 2 vols. oxygen. This is the nature of fire-damp. It is a mixture of this gas with air. If the air is less than six times, or more than fourteen times the volume of the gas, explosion does not take place.

To put an end to the frightful accidents formerly so common in coal mines, Davy invented his safety lamp, which is only a common oil-lamp, surrounded by wire gauze. Davy found that flame, which is incandescent gaseous matter, and intensely hot,

could not pass through fine wire gauze, the gaseous matter being cooled by the contact with the metal, below the point at which it becomes luminous. Now, as it requires the heat of flame to fire the explosive mixture, it is evident that the flame of the lamp, not being able to pass through the wire-gauze as flame, but only as gaseous matter not incandescent, cannot fire the mixture which surrounds it. Since this beautiful contrivance was adopted, explosions have become much more rare in coal-mines; and there is good reason to believe that such as have occurred have arisen from neglect of the use of the safety-lamp, or from carelessness in using lamps, the gauze of which has been so injured by blows, or otherwise, as to allow the flame to pass. In the dreadful explosion at the Lundhill colliery, in the present year (1857), it was proved that gross neglect of the necessary precautions had rendered the mine at all times liable to explosions. The lamps were used without the gauze cover. It is so difficult to prevent this at all times, that some contend that safety is only to be ensured by constant ventilation, carried on by means independent of the miners.

When an explosion takes place, those who are not burnt or shattered, are generally suffocated by the carbonic acid, which is the product of the explosion.

Marsh gas,  $C_2H_4$ , is considered to be the hyduret, or hydride of methyle,  $C_2H_3$ , and its rational formula is  $C_2H_3, H$ . It is the first member of a very remarkable series, that of the hydrides of the methylic or ethylic radicals, in organic chemistry. In such a series, called a homologous one,  $C_2H_2$  is added at each step. As hydrogen,  $H$ , may be considered the foundation of the series of the methylic radicals, so analogous to hydrogen and metals in their relations; so the foundation of the marsh gas series may be supposed to be a double molecule of hydrogen,  $HH$ . Thus we have,

- |  |            |                   |                                 |
|--|------------|-------------------|---------------------------------|
| 1. Hydride of hydrogen                 | . . .      | $HH$ .            | This, + $C_2H_2$                |
| = 2. Marsh gas, or hydride of methyle, | $C_2H_3$ , | $H$ or $C_2H_4$ . | This, + $C_2H_2$                |
| = 3. Hydride of ethyle                 | . . .      | $C_4H_5$ ,        | $H = C_4H_6$ . This, + $C_2H_2$ |
| = 4. Hydride of propyle                | . . .      | $C_6H_7$ ,        | $H = C_6H_8$ , and so on.       |

The lower members of the series are gaseous; after which come liquids, the lower very volatile, the higher less so; then solids; the lower more fusible and volatile, the higher less so. There can be no doubt that several of all these forms occur among the products of the destructive distillation of organic matter, such as wood or coal; that the gases occur in coal gas, with the vapours of the more soluble fluids; that the fluids are found in the liquids called naphthas and paraffine oils, and that the solids of this

series constitute part of the bodies which have been named paraffines.

This series of carbo-hydrogens is not acted on by chlorine in the dark.

b. Olefiant Gas.  $C_2H_2 = 14$ ; or,  $C_4H_4 = 28$ .

This gas occurs in the gaseous mixture of coal-mines, mixed with the preceding. It is prepared by heating 1 part of strong alcohol with 4 parts of oil of vitriol. The mixture blackens and gives off the gas, which may be collected over water. It is rendered quite pure by passing it through oil of vitriol, which removes some of the vapour of ether which is generally present.

It may also be obtained more conveniently, as the mixture above mentioned is apt to thicken, from carbonaceous matter being separated, and to froth over, either by adding sand to the alcohol and sulphuric acid, so as to form nearly a solid mass, or by heating to about  $325^\circ$ , its boiling point, a mixture of oil of vitriol with one-third of its weight of water, and causing a stream of alcohol to flow into the flask so that the temperature continues the same. The acid first forms, in all these processes sulphovinic acid,  $C_4H_5O$ ,  $HO$ ,  $2SO_3$ , with the alcohol, and this is resolved into olefiant gas and oil of vitriol;  $C_4H_5O$ ,  $HO$ ,  $2SO_3 = C_4H_4 + 2(HO, SO_3)$ . The same quantity of acid will decompose an almost unlimited amount of alcohol.

Olefiant gas is transparent and colourless. When brought in contact with a flame in the air, it takes fire, and burns with a very luminous white flame. Mixed with its volume of chlorine, the two gases rapidly disappear, producing an ethereal or oily liquid,  $C_4H_4Cl_2$ ; hence the name. But if mixed with 2 vols. of chlorine, and set fire to, the mixture burns off with a red flame, and an immense quantity of smoke, which is carbon deposited in the solid form, the hydrogen uniting with the chlorine,  $C_4H_4 + Cl_4 = 4HCl + C_4$ .

When a light is applied to a mixture of 1 vol. of olefiant gas, and 3 vols. of oxygen, or 15 vols. of air, a very violent explosion takes place, the products being carbonic acid and water,  $C_4H_4 + O_{12} = 4CO_2 + 4HO$ .

Olefiant gas,  $C_4H_4$ , is the type of a second remarkable series of carbo-hydrogens, that of the hydrides of the acetylic series of negative radicals. It is, however, not the first member of the series, for that is the hydride of formula  $C_2H_2$  or  $C_2H$ ,  $H$ , a body not very well known as yet. In this series we have

|                           |   |
|---------------------------|---|
| Hydride of formyle        | . $C_2H$ , $H$ , or $C_2H_2$ , which, with $C_2H_2$     |
| is = Hydride of acetylene | . $C_4H_2$ , $H$ , or $C_4H_4$ ; and this with $C_2H_2$ |
| is = Hydride of tritylene | . $C_6H_2$ , $H$ , or $C_6H_6$ , and so on.             |

The properties of the members of this series are very similar to those of the marsh gas series ; but, from containing more carbon, those of the olefiant gas series burn, in general, with a more luminous flame. They are also absorbed by chlorine in the dark.

They are formed in destructive distillations, and are consequently found mixed with the marsh gas series ; the lower members, as in that series, being gaseous, the middle ones liquid, the higher solid. Some of the naphthas and paraffine oils belong, no doubt, to this series, as well as some of the so-called paraffines. In the higher part of the scale, there is but little difference of composition between the two series. Thus paraffine has been said by some to be  $C_{60}H_{60}$ . This is a member of the olefiant gas series. But the corresponding member of the other series is  $C_{60}H_{62}$  and is also a body like paraffine.

#### CARBON AND NITROGEN.

Cyanogen.  $C_2N = Cy = 26$ .

These elements in the nascent state, and in the presence of a base, combine to form a very remarkable compound, which, from being a chief ingredient in Prussian blue, has been called Cyanogen. This compound is best obtained by heating a mixture of 6 parts of dried ferrocyanide of potassium, and 9 parts of bichloride of mercury in a flask, when cyanogen is given off in the form of a colourless gas, absorbed by water, having a very pungent and peculiar smell. Its Sp. G. is about 1.81. Cyanogen gas is combustible, and burns with a beautiful purplish red flame. It is liquefied by a pressure of 3 or 4 atmospheres, and the liquid is frozen to a crystalline mass by a cold of  $-32^{\circ} F$ .

Such are the leading external properties of this remarkable compound, which, in its chemical relations, however, acts most frequently the part of a simple acid radical, entirely analogous to chlorine, bromine, iodine, or fluorine, forming an acid with hydrogen, and neutral salts with metals.

In fact, cyanogen is the type of the important class of compound acid radicals, which characterise the chemistry of organic bodies, although, as we have seen, they also occur in inorganic chemistry. But as cyanogen is exclusively a product of organised compounds, or of the destruction of organic bodies, the detailed description of its chemical relations, and of its numerous compounds, belongs to organic chemistry.

The composition of cyanogen is  $C_2N$  ; but as it plays the part of an elementary body, it is generally more convenient to employ for it the symbol Cy.

Carbon and nitrogen are supposed to form another compound, which is also a compound radical, and is called Mellone. Symbol, Me. It will be described in the organic chemistry.

#### CARBON AND CHLORINE.

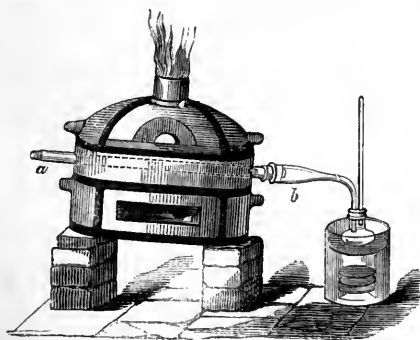
Carbon does not directly unite with chlorine; but when chlorine is made to act on certain organic compounds, which are decomposed by it, the carbon being presented to it in the nascent state, combines with the chlorine. There are several chlorides of carbon: 1. Dichloride of carbon,  $C_2Cl_4$ , a white solid fusible and combustible body. 2. Protochloride of carbon,  $CCl_4$ , a liquid, boiling at  $160^\circ$ . 3. Perchloride of carbon,  $C_2Cl_6$ , a very fusible solid, boiling at  $360^\circ$ , combustible. None of these compounds have any practical interest.

Little, if anything, is known of the compounds of iodine, bromine, and fluorine, with carbon.

#### CARBON AND SULPHUR.

Bisulphide of Carbon,  $CS_2 = 38$ .

This compound is best formed, on the small scale, by filling with fragments of recently ignited charcoal a wide cast-iron tube, which is placed in a somewhat inclined position across a



furnace, as in the figure. The lower end of the tube is connected with a cooling apparatus, the wide glass tube of which is kept cold by iced water, and terminates in a two-necked bottle, also placed in ice-cold water; a tube in the second tubulature of the

bottle, allows the escape of gaseous matter. The part of the iron tube containing the charcoal being now raised to a red-heat, a fragment of sulphur is introduced into the upper end, which is instantly closed. The sulphur melts, boils, and passes in vapour over the hot charcoal, which combines with it, forming bisulphide of carbon, which condenses in the bottle as a volatile liquid. A second fragment of sulphur is introduced very soon after the first; and if the proportion of



sulphur introduced at once, and the heat of the charcoal be fortunately observed, a large quantity of the new compound may soon be obtained. The gases disengaged appear to be a gaseous sulphuret of carbon, chiefly formed when there is too little sulphur, and sulphuretted hydrogen, arising from the presence of hydrogen or water in the charcoal.

The bisulphide of carbon is purified by distillation at a very gentle heat, and then forms a very transparent, mobile, colourless liquid, of Sp. G. 1.272, sinking therefore in water, and it has a peculiarly offensive smell of putrid cabbage. It is very volatile, boiling at  $118.5^{\circ}$ ; and very combustible, burning with a pale blue flame, and producing sulphurous and carbonic acids. It is insoluble in water, soluble in alcohol, ether, and oils. It dissolves sulphur and phosphorus readily; and these solutions, by spontaneous evaporation, yield fine crystals of those elements. It also dissolves camphor, essential oils, and resins. It is considered a sulphur acid, as it combines with protosulphurets to form sulpho-salts, called sulpho-carbonates.

Bisulphide of carbon is occasionally used as an external application in burns; and it promises to be useful as a solvent for resins, many of which it dissolves readily, and thus forms varnishes, which, from its great volatility, dry very rapidly.

## 12. BORON. $B = 10.9$ .

This element is found, in combination with oxygen, forming boracic acid in certain hot springs in the north of Italy; and as biborate of soda (borax), on the shores of some lakes in Thibet.

From boracic acid, boron is with difficulty obtained by the action of potassium, aided by heat, which removes the oxygen. Or it may be prepared by the action of potassium on borofluoride of potassium, when boron is separated.  $KF, BF_3 + K_3 = 4KF + B$ . The fluoride of potassium which is formed, is dissolved away by water, and the boron remains as a dark olive-coloured powder. Boron is fixed in the fire, but if heated in oxygen gas, it burns brilliantly, being converted into boracic acid.

Boron, like carbon, occurs in three allotropic forms. That modification which corresponds to the diamond is very brilliant and very hard.

Boron and Oxygen. Boracic Acid,  $BO_3 = 34.9$ .

When boron is heated in air it burns like tinder, or as above stated, if heated in oxygen, with a brilliant light, and yields this acid. It is obtained by evaporating the hot springs of Sasso, in Italy, in a somewhat impure state, under the name of Sassoline, or crude boracic acid. It is best prepared by dis-

solving borax in four parts of hot water, and adding to the hot solution one-third of the weight of the borax of oil of vitriol. Borax is a baborate of soda; the sulphuric acid takes the soda, forming a soluble salt, and the boracic acid is set free. Being very sparingly soluble in cold water, it is deposited, on cooling, in scaly crystals, which are a crystallised hydrate of boracic acid,  $\text{BO}_3 + 3\text{HO}$ . These crystals are purified by being dissolved in the smallest possible quantity of boiling water after they have been washed with a little cold water. On cooling, this solution deposits pure hydrated boracic acid.

When the crystals are heated to  $212^\circ$ , they lose half the water they contain, and this is probably water of crystallisation. The residue is  $2\text{BO}_3 + 3\text{HO}$ ; so that the original crystals may be represented as  $2\text{BO}_3 + 3\text{HO} + 3\text{aq}$ . When heated to redness the acid melts, and on cooling forms a transparent brittle glass. It is quite fixed in the fire in close vessels if dry; but it volatilises readily with the vapour of water, so that a solution of boracic acid cannot be evaporated without notable loss. It is in this way, along with steam, that it is brought from great depths into the springs in which it is found.

Boracic acid is sparingly soluble in cold, readily in hot water. It is very soluble in alcohol, and its alcoholic solution burns with a flame mixed and tinged with pale green: a property characteristic of the compounds of boron.

It is a feeble acid, and reddens litmus slightly: it colours turmeric brown, like an alkali. With bases it forms salts called borates, which are for the most part insoluble. The alkaline borates alone are soluble. All the salts of this acid are very fusible, and promote the fusion of other bodies when mixed with them. Hence, borax is much used as a blow-pipe flux, which not only promotes fusibility, but at a red-heat dissolves siliceous compounds to a clear, fusible glass.

No compound is known of boron with hydrogen. When anhydrous borax is heated with sal-ammoniac, nituret of boron, BN, is formed. It is a white powder, which feels like talc.

With chlorine boron combines when it is heated in the gas, or when chlorine is passed over a red-hot mixture of boracic acid and charcoal. The terchloride of boron,  $\text{BCl}_3$ , is a gas at ordinary temperatures. It has a pungent acid smell, and forms thick vapours in the air. These are the results of its action on the water of the atmosphere, whereby hydrochloric and boracic acids are formed:  $\text{BCl}_3 + 3\text{HO} = 3\text{HCl} + \text{BO}_3$ .

Nothing is known of the compounds of boron with bromine and iodine.

## BORON AND FLUORINE.

Terfluoride of Boron.  $\text{BF}_3 = 67.6$ .

Boron has a remarkable affinity for fluorine, and when fluor-spar (fluoride of calcium) is heated to redness with boracic acid, a gaseous compound is produced, analogous in composition and properties to the terchloride of boron.  $3\text{CaF} + 4\text{BO}_3 = 3(\text{CaO}, \text{BO}_3) + \text{BF}_3$ . The Sp. G. of the gas is 2.36. It instantly seizes on water, decomposing it, and thus, like the terchloride, forms very thick vapours with the moisture of the air. It is, in fact, a very delicate test of the presence of moisture in any gas.

When this gas is absorbed by water to saturation, hydrofluoric acid and boracic acid are formed:  $\text{BF}_3 + 3\text{HO} = 3\text{HF} + \text{BO}_3$ . The hydrofluoric acid unites with the boracic acid and 1 eq. of water, forming an acid,  $3\text{HF} + \text{HO}, \text{BO}_3$ , and this, when acted on by bases, yields salts, the formula of which is  $3\text{MF} + \text{MO}, \text{BO}_3$ . Berzelius has shown that when terfluoride of boron is absorbed by concentrated hydrofluoric acid, another compound is formed, the formula of which is  $\text{HF} + \text{BF}_3$ . It is an acid, the formula of its salts being  $\text{MF} + \text{BF}_3$ . All its salts, when heated, give off terfluoride of boron.

Boron, when heated in the vapour of sulphur, burns and forms a sulphuret of boron, which is a white solid decomposed by water, with which it yields sulphuretted hydrogen and boracic acid.

13. SILICON.  $\text{Si} = 21.3?$ 

This element is, with the exception probably of oxygen, the most abundant of all those which form the solid mass of our earth. It occurs, however, only in a state of combination with oxygen, as silicic acid or silica, which is a chief ingredient of all rocks, except limestone, rock-salt, and coal, and also of all soils.

Silicon is best obtained by heating potassium with silicofluoride of potassium,  $3\text{KF} + 2\text{SiF}_3$ , which, with 6 eqs. of potassium yields  $9\text{KF} + \text{Si}_2$ . Water dissolves off the fluoride of potassium, and leaves the silicon as a dark brown powder, which contains some hydrogen, and is purified by exposure to a low red-heat. Silicon is infusible, and after having been ignited in close vessels it is so compact as not to burn when heated even in oxygen. It is also much denser, and is considered to be an allotropic modification, Sig. A third form has been described, in shining scales like platinum filings. This will be  $\text{Si}_\gamma$ . It is

not acted on by any acid except the hydrofluoric acid, which slowly dissolves the ordinary variety ; while a mixture of nitric and hydrofluoric acids is required to dissolve  $\text{Si}\beta$ . When silicon is fused with nitrate or carbonate of potash, it is oxidised with a smart deflagration. It is heavier than oil of vitriol, at least in the form of  $\text{Si}\beta$ .

#### SILICON AND OXYGEN.

Silicic Acid.  $\text{SiO}_2 = 45.3 ?$

**SYN. Silica.**—This acid is found pure in rock crystal, or in white quartz. Along with small and variable quantities of certain metallic oxides it forms many well-known minerals—as yellow or smoke rock crystal with oxide of iron ; agate, jasper, heliotrope, carnelian, with the same metal ; amethyst with oxide of manganese ; prase with oxide of nickel ; rose-quartz with some fugitive colouring matter ; opal and calcedony with water, &c., &c. Many sands and sandstones are nearly pure silica, and quartz rock and flint are quite pure.

Silicic acid may be obtained in a state of purity, from any siliceous sand, by fusing it with three or four parts of carbonate of potash, dissolving the fused mass in water, adding hydrochloric acid, which separates the silica as a jelly, which is a hydrate of the acid, and evaporating the whole to dryness. Water removes from the dry mass all soluble chlorides, and leaves the silica, which, when dried, is a snow-white powder, insoluble in water, and all acids except the hydrofluoric acid. It dissolves in caustic or even carbonated alkalis with the aid of heat. Silica has a Sp. G. of 2.6, and in hardness approaches the precious stones. It is fusible in the oxyhydrogen blow-pipe, and may be drawn into threads. It is slowly volatilised in a current of steam at a high temperature, and is thus carried into the throat of furnaces in concretions like calcedony.

Silicic acid combines with bases, forming silicates, all of which, except those containing an excess of the stronger alkalis, are insoluble in water. The greater number of rocks and minerals consist of silicates, especially those of alumina, lime, magnesia, oxide of iron, potash, and soda. The silicates of potash and soda, when heated to redness, form glass, which when the acid predominates is insoluble, and is the basis of all ordinary glass, which contains, besides potash or soda, lime, magnesia, or oxide of iron ; when the alkali is in excess, the glass is very soluble in water. Many silicates found in nature, as the zeolites, are soluble in strong acids ; but most of them lose their solubility

on being ignited. Many, such as felspar, are not attacked by acids, even before ignition.

Silicic acid occurs both in the animal body and in the ashes of plants, especially of gramineæ. Many of the lower vegetable or doubtful organisms are chiefly formed of it. Thus the whole tribe of diatomaceæ consist of cells having firm siliceous walls. As these are indestructible, the remains of the diatomaceæ often form large beds of nearly pure silicic acid. The spicules and gemmules of sponges, as well as the shells of the polycystineæ, and other organisms, are also siliceous.

The equivalent of silicon and the formula of silicic acid are much disputed. Berzelius adopted the equivalent we have given, and considered silicic acid as a teroxide,  $\text{SiO}_3$ . But of late it has been maintained, that the acid is a binoxide,  $\text{SiO}_2$ , which, as its composition is known, makes the equivalent of silicon 14.24. It would seem that this view yields simpler formulæ for the numerous silicates occurring in the mineral kingdom. We have only space to indicate this. On the other hand, on the view of Berzelius, felspar is analogous to alum, being  $\text{KO}$ ,  $\text{SiO}_3 + \text{Al}_2\text{O}_3$ ,  $3\text{SiO}_3$ ; and it is not easy to see how the formula  $\text{SiO}_2$ , with its atomic weight, can be applied to this mineral.

No compounds are known of silicon with hydrogen or nitrogen.

#### SILICON WITH CHLORINE AND BROMINE.

When silicon is heated in chlorine it burns and forms a compound, which is better prepared by passing chlorine over a red-hot mixture of silicic acid and charcoal,  $\text{SiO}_3 + \text{C}_3 + \text{Cl}_3 = \text{SiCl}_3 + 3\text{CO}$ . The compound, which is called terchloride of silicon, condenses in the cold part of the apparatus as a very volatile, pungent, and colourless liquid, which decomposes water, forming hydrochloric and silicic acids:  $\text{SiCl}_3 + 3\text{HO} = 3\text{HCl} + \text{SiO}_3$ .

Bromine yields an analogous terbromide,  $\text{SiBr}_3$ , the properties of which are similar to those of the terchloride.

Iodine is not known to combine with silicon.

Silicon and Fluorine.  $\text{SiF}_3 = 78$ .

Silicic acid is rapidly dissolved by hydrofluoric acid, and a gas is produced, which is found to be a terfluoride of silicon:  $\text{SiO}_3 + 3\text{HF} = 3\text{HO} + \text{SiF}_3$ . This gas is best obtained by heating a mixture of powdered fluor-spar and quartz with oil of vitriol:  $3\text{CaF} + \text{SiO}_3 + 3(\text{HO}, \text{SO}_3) = 3(\text{CaO}, \text{SO}_3) + 3\text{HO} + \text{SiF}_3$ . The gas must be collected over mercury. It is colourless, fuming strongly in the air, its Sp. G. 3.66. It is absorbed by water, and

hydrated silicic acid is deposited, while an acid is found in the water composed of  $3\text{HF} + 2\text{SiF}_3$ . With bases this acid forms salts, called silicofluorides, the formula of which is  $3\text{MF} + 2\text{SiF}_3$ . These salts are nearly all insoluble, and when heated give off terfluoride of silicon.

The aqueous hydrofluosilicic acid is used in chemistry to separate potash, with which it forms an insoluble salt, from certain acids such as chloric acid, by which means these acids are obtained in the free state. It is also used as a test, to distinguish between compounds of barium and of strontium, as it forms after a short time a crystalline deposit in the solutions of the former base only.

Heated with sulphur, silicon combines with it, forming a white earthy compound,  $\text{SiS}_3$ . It decomposes water, yielding sulphuretted hydrogen and silicic acid :  $\text{SiS}^3 + 3\text{HO} = 3\text{HS} + \text{SiO}_3$ .

## METALS.

## GENERAL OBSERVATIONS ON METALS.

IN the arrangement we have adopted, all the elements not hitherto described are considered metals, although some of them especially arsenic and tellurium, are, in many points, very analogous to the metalloids. The metals are at present 50 in number. See the list of elements, page 2.

A metal is defined to be a body possessing the peculiar appearance called the metallic lustre (which is well illustrated in polished silver or in mercury), and capable of conducting well both heat and electricity. All the metals possess this combination of characters, but in other physical characters they exhibit great variety. We shall notice the following :—Specific Gravity, Hardness, Tenacity, Fusibility, and Volatility.

1. Specific Gravity. The density of metals varies from 0.5936 (water being = 1) to 22 : the former being the Sp. G. of lithium, the latter that of platinum. Iridium is said to be still denser than platinum, its density, according to some, being as high as 26 ; but this is doubtful.

2. Hardness. Some metals, as potassium, lead, tin, silver, &c., are so soft as to be easily cut with a knife ; potassium and sodium may even be kneaded in the fingers. Others, such as iron, nickel, antimony, &c., are much harder ; and a few, such as rhodium and iridium, especially the latter, possess a very high degree of hardness.

3. Tenacity. This property is present in very various degrees in metals. Some, as antimony, bismuth, cobalt, have so little tenacity that they are brittle and may be powdered ; while others may be beat out into thin leaves, or drawn into fine wires. Those two forms of tenacity, malleability and ductility, are not always proportional to one another ; for iron, which can only be beat into plates of a very moderate thinness, being of all the malleable metals, the least malleable, may be drawn out into very fine wires, and is among the most ductile of metals. Of the malleable metals, the following are remarkable : lead, tin, copper, palladium, platinum, silver and gold. The last-named metal may be beat out into leaf so fine, that, although quite entire and free from visible pores, 57 square inches of the finest

gold leaf will not weigh more than one grain. Zinc, which is rather brittle at ordinary temperatures, admits of being rolled into thin plates at 300° and 400°. The most ductile metals are lead, copper, palladium, iron, silver, gold, and platinum: 1 grain of gold may be drawn out into a wire 550 feet long, and platinum is about 6 times more ductile, according to Wollaston. Iron wire, although not the finest, is very fine, especially if the metal be pure, and is stronger than wire of equal diameter of any other metal.

4. Fusibility. One metal, mercury, is liquid at all temperatures above —39° F., and below 660°. Some, such as potassium, sodium, &c., melt at a very moderate heat; others, such as lead, tin, &c. at temperatures below red-heat; others at a strong red or white heat, such as copper, silver, and gold. Some, as platinum, require the heat of the oxyhydrogen blow-pipe to melt them; and one at least, iridium, appears to resist, when pure, even this intense heat.

5. Volatility. Some metals are very volatile, compared with others. Mercury volatilises slowly at all temperatures above 80° or 100° F., and below its boiling point, at which temperature, 662°, it is rapidly converted into vapour. At the other extreme is iridium, which is quite fixed, not even melting in the strongest white heat yet known. The following metals are converted into vapour, or they boil, at temperatures varying from a low to a bright red-heat; cadmium, zinc, arsenic, tellurium, potassium, and sodium. Most of the others are fixed, although some of them, in the flame of the oxyhydrogen blow-pipe, appear to be volatilised in small quantity.

6. Elasticity and Sonorousness. Several of the metals, especially such as are hard, are elastic, and, when struck, give out a clear ringing sound. But it is chiefly in alloys, or compounds of two or more metals, that these qualities are developed, Steel, which is a carburet, or carbide of iron, is remarkably elastic, and is therefore used for springs. The amount of carbon is so small, that steel is generally spoken of as metallic. But iron is equally modified by very minute quantities of other metals. Thus iron, with a very little zinc, antimony, or tin, becomes more fusible, yet harder, and even harder than steel. Silver is very sonorous, but bell-metal, remarkable for this property, is an alloy of copper and tin. Iron, alloyed with a certain proportion of copper and zinc, yields an alloy, even more sonorous than bell-metal. Bells of this alloy, in which the proportion of iron is very large, give a beautiful tone, but have one disadvantage, that they must be thicker, and consequently heavier than bells of equal diameter of bell-metal.



The chemical relations of metals are very important ; and as there runs through the whole class a great analogy in this respect, it is advisable to describe, generally, the chemical characters of metals ; by which means we are enabled to render the account of the individual metals more brief and more easily remembered.

Metals have powerful affinities, especially for the metalloids, with almost all of which they combine, and frequently in several proportions. In addition, therefore, to the important uses of the metals, as such, the useful applications of a large number of metallic compounds are of the highest interest and value.

Almost all the metals have a powerful affinity for oxygen, and all of them may be made to combine with it. In like manner the metals have strong affinities for, and may easily be made to combine with chlorine, bromine, iodine, fluorine (to which may be added cyanogen), as well as sulphur, selenium, and in many cases, phosphorus and carbon ; in a few, hydrogen and silicon. Metals also combine with each other, and of late many metals have been ascertained to form very interesting compounds with organic molecules, such as methyle, ethyle, &c. Owing to the extensive range of these affinities, metals are rarely found uncombined, or native, as it is called in nature, and the operations of metallurgy are chiefly such as are required to separate metals from the compounds in which they occur, which are called their *ores*. Oxygen, in the atmosphere and in water, being far more abundant than the other metalloids, and having a very powerful affinity for metals, they are chiefly found oxidised, and are therefore commonly extracted from the ores by the process of deoxidation, or reduction, as it is termed. Many metals, however, such as lead, copper, bismuth, mercury, &c., are obtained almost entirely from natural sulphurets, or sulphides.

The great mass of the earth's crust, so far as known, consists of various rocks in which, for the most part, silicic acid is combined with the oxides of various metals. Of such silicates, felspar is the most important ; it is one of the three minerals in granite, the two others being quartz, or silicic acid, and mica, another silicate. The well-known rocks gneiss, mica-slate, and clay-slate, contain the same minerals, the proportion of felspar increasing in the order named. Felspar occurs also in syenite, porphyry, granwacke, and many other rocks. It contains the two metals, potassium and aluminium, which are therefore, very abundant. Limestone, marbles, and chalk, consist of the carbonate, gypsum of the sulphate, of lime, or oxide of calcium. Magnesian limestone is a double carbonate of calcium and

magnesium. Clay beds contain chiefly alumina, the sesquioxide of aluminium, with some silica and a little potash, being derived from the action of the weather on felspar; and felspar is also the chief constituent of basaltic and volcanic rocks. Rock-salt consists of chloride of sodium, which also exists in prodigious quantity in sea-water. Lastly, oxide of iron, is almost universally present, in greater or less proportion, in nearly all rocks and soils.

It will be observed, that all the metals here enumerated, except iron, are such as are with difficulty obtained in the metallic state, from their intense attraction for oxygen, &c. Of the useful metals the following only are found uncombined, or in the metallic state: platinum, gold, silver, mercury, and copper, the latter metal only occasionally. Metallic iron also occurs in masses, which, there is every reason to believe, are always of atmospheric origin, or *aërolites*. They always contain traces of cobalt, nickel, and sulphur: often also chromium and arsenic. This iron is very hard and tough, but perfectly malleable.

The ores from which, as already mentioned, most of the useful metals are obtained, and which are chiefly oxides and sulphides, occur scattered and in relatively small quantity, but fortunately for us, they are in general collected in beds, as is the case with the carbonate of iron, which forms layers of great extent in the coal formation, or in veins, which traverse various rocks, usually in directions approaching, more or less, to the vertical. In such veins occur the ores of silver, mercury, copper, lead, zinc, tin, antimony, bismuth, arsenic, &c. It is more than probable, that the metallic ores have been thus separated, and as it were, concentrated, by the long continued action of weak electric currents.

#### METALS WITH OXYGEN.

Metals differ in the degree of their attraction for oxygen. Some metals, such as potassium, rapidly combine with oxygen when exposed to the air, or when brought in contact with water or with any other oxidised compound. Others, such as iron, are very slowly oxidised by exposure to the air at ordinary temperatures, and hardly act on cold water: but at a strong red-heat they burn in the air, and decompose the vapour of water, setting free hydrogen gas. Others again combine with oxygen when heated in air, but do not decompose water at all, such as copper. These, as well as the preceding, are in general easily oxidised by acids; and their attraction for oxygen is such that their

oxides, once formed, are not decomposed by a red-heat alone, without the help of combustible matter. Finally, some metals, such as gold and silver, &c., have much less attraction for oxygen. They are not so easily or directly oxidised, and the oxides once formed, are quite easily decomposed by a red-heat, being resolved into metal and oxygen.

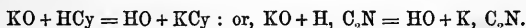
When metals combine with oxygen, they form three classes of oxides.

1st. Bases, or basic oxides, the most usual formula of which is  $MO$ ; such oxides are called protoxides. Besides protoxides a pretty numerous class of basic oxides has the formula  $M_2O_3$ . these are sesquioxides. A very few oxides have the formula  $MO_2$ : these are binoxides or deutoxides. They are usually neutral or indifferent. Potash  $KO$ , is an example of a protoxide; sesquioxide of iron,  $Fe_2O_3$ , of a sesquioxide; and superoxide of lead,  $PbO_2$ , of a deutoxide.

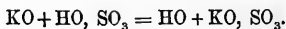
All basic oxides form neutral salts by combining with acids. In all such cases there is produced, besides the neutral salt, a quantity of water, the oxygen of which, according to the most probable view, is derived from the metallic oxide. Its hydrogen must therefore be derived from the acid, and in the case of the hydrogen acids with simple radicals, this is admitted by all. For example, when potash,  $KO$ , acts on hydrochloric acid,  $HCl$ , the change is universally admitted to be as follows:—



That is, the basic oxide, and the hydrogen acid, give rise to water and to chloride of potassium, both neutral substances. Neither have we any difficulty in adopting the same view in the case of a hydrogen acid with a compound radical; for example hydrocyanic acid:—

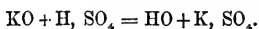


But when we bring potash in contact with oil of vitriol or strong sulphuric acid, some chemists are inclined to adopt a different explanation of phenomena precisely analogous. They call the acid hydrated sulphuric acid,  $HO, SO_3$ , and express the action as follows:—



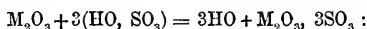
Here, it will be observed, the results are quite similar to those in the preceding cases; namely, the separation of water, and of a neutral salt, in this case sulphate of potash. And yet we adopt a different explanation, at least on the older view of acids and salts, supposing the water to pre-exist in the acid, and to be

replaced by the oxide. As it is, however, quite unphilosophical to employ two explanations of analogous facts if one will suffice, we are thus induced to prefer the newer view of acids and salts formerly alluded to, which admits of our giving the same explanation of the two cases. According to this view, then, we consider oil of vitriol a hydrogen acid,  $H, SO_4$ , and express the change thus :—

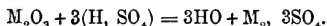


On comparing this with the equation above given for the action of potash on hydrocyanic acid in its second form, it will be seen that the analogy is perfect. Both acids and both salts contain a compound acid radical, in the one case  $C_2N$ , in the other  $SO_4$ ; and both differ from the acid and salt of chlorine in the fact of their radicals being compound, or rather *known to be* compound; for chlorine may very possibly be itself a compound radical, although at present we must view it as simple, because it is undecomposed.

The action of a basic sesquioxide on an acid, say sulphuric, is represented as follows on both the different theories of acids :—



or,



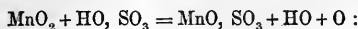
Here we see that, for every equivalent of oxygen in the base, an equivalent of acid is required to form a neutral salt; and that, on the new view, the resulting neutral salts are compounds corresponding to the basic oxides from which they are formed. Thus we have—

| Basic Oxide. |     | Corresponding Neutral Salt. |                              |
|--------------|-----|-----------------------------|------------------------------|
| $M + O$      | . . | $M + SO_4$ ,                | or in general terms, $M + R$ |
| $M_2 + O_3$  | . . | $M_2 + 3SO_4$               | „ „ $M_2 + R_3$              |

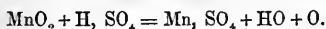
Such are the most important chemical relations of the basic oxides, which include, among the protoxides, the strongest alkalies and alkaline earths.

2nd. Neutral or indifferent metallic oxides. These appear, by combining with an additional quantity of oxygen, to have lost the basic, without acquiring the acid character. They commonly enter into few combinations of any kind. Their composition varies, being sometimes  $M_3O_4$  and sometimes  $MO_2$ . Red oxide of lead,  $Pb_3O_4$ , is an example of the former; peroxide of manganese,  $MnO_2$ , and superoxide of lead,  $PbO_2$ , of the latter. When heated with acids, oxygen is given off, while

a basic oxide is formed, and acts on the acid as above, forming a neutral salt. Thus, peroxide of manganese, heated with oil of vitriol, gives—

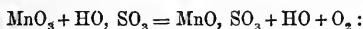


or,

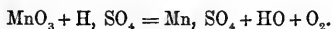


3rd. Metallic acids. These are pretty numerous. When the same metal forms a basic oxide and an acid, the latter always contains more oxygen. There are several different formulæ among metallic acids. They are sometimes deutoxides, as titanous acid,  $\text{TiO}_2$ ; very often teroxides, as chromic acid,  $\text{CrO}_3$ ; manganic acid,  $\text{MnO}_3$ , arsenious acid,  $\text{AsO}_3$ , and others; in two cases there are 5 eqs. of oxygen, as in arsenic acid,  $\text{AsO}_5$ , and antimonous acid,  $\text{SbO}_5$ ; in one case the ratio of 2 to 7, as in permanganic acid,  $\text{Mn}_2\text{O}_7$ ; and in one case a quadroxide, as osmic acid,  $\text{OsO}_4$ .

Metallic acids, when heated, generally lose oxygen, and are reduced to the basic oxide; this takes place especially if they are heated with acids. Thus manganic acid,  $\text{MnO}_3$ , heated with sulphuric acid, yields oxygen gas and neutral sulphate of the protoxide.



or,



When we wish to form metallic acids, we commonly heat or deflagrate the metal, or its lower oxides, along with an alkaline nitrate or chlorate, in which case the acid that is formed remains in combination with the alkali. Or chlorine gas is passed through water in which the oxide, in fine powder, is suspended; sometimes along with an alkali, sometimes alone.

When our object is to deprive metals of the oxygen with which they are combined, or to reduce them, as it is called, to the metallic state, different methods are followed, according to the attraction of metal for oxygen.

1. The oxides of the noble metals, such as mercury, silver, gold, platinum, &c., are reduced by a red-heat alone.

2. The oxides of a large number of metals, such as copper, iron, tin, barium, or potassium, can only be reduced by the united action of heat and combustible matter, such as carbon, hydrogen, &c. The change is as follows:  $\text{MO} + \text{C} = \text{M} + \text{CO}$ ; or  $\text{MO} + \text{H} = \text{M} + \text{HO}$ . In the former case carbonic oxide gas, in the latter water, is produced, and being expelled by the heat,

leaves the metal pure. The use of carbon for reduction is the foundation of all the metallurgic processes on a large scale. As the ores, however, are not pure, substances called fluxes are added to cause the impurities to melt, forming a fluid glass, below which the melted metal is found.

Perhaps the most powerful reducing or deoxidising compounds at a red-heat are the formiates, and cyanide of potassium. The formula of a formiate is  $\text{MO}$ ,  $\text{C}_2\text{HO}_3 = \text{MO} + \text{HO}$ ,  $2\text{CO}$ : so that it yields at a red-heat carbonic oxide gas, a body having much attraction for oxygen. Cyanide of potassium is  $\text{KCy} = \text{K}, \text{C}_2\text{N}$ ; and, as Liebig has pointed out, it combines the very powerful deoxidising agency of carbon and of potassium. Its reducing power is very great.

3. The oxides of the metals of some of the alkalies and earths, whose attraction for oxygen is very strong, and which are with difficulty reduced in any other way, are decomposed by a powerful galvanic battery so as to yield the metals. This is only done on a very small scale.

4. Many oxides in solution are reduced to the metallic state by other metals having a stronger attraction for oxygen, which take the place of the metal previously in solution. Thus copper precipitates silver, and iron precipitates copper.

5. Many oxides in solution, that is, combined with acids, are reduced to the metallic state by what are called deoxidising agents. Thus, the noble metals, such as gold, platinum, &c., are reduced by sulphurous, phosphorous, and hypophosphorous acids and their salts; by oxalic and formic acids and their salts: gold is even reduced by hydrogen gas and by solutions of protosalts of iron, such as green vitriol. In all these cases the reducing or deoxidising agent is oxidised; phosphorous acid, for example, yielding phosphoric, and protoxide of iron passing into peroxide, at the expense of the metallic oxide.

The electrotype, in which copper, silver, gold, or platinum are reduced to the metallic state in such a way as to form coherent masses similar to the hammered metals, and by which the most beautiful and perfect copies of medals may be taken, is a process depending partly on the reducing agency of the galvanic battery, partly on that of hydrogen gas, which, instead of escaping uncombined at the negative pole, is then oxidised at the expense of the metallic oxide. In this process, which has already been briefly described, when treating of decomposition by the electric current, it is essential that the electric current should be slow and uniform, otherwise the metal is deposited in different states. Plating and gilding by this process have a beautiful appearance, and have now been brought

to great perfection. Certain double cyanides of silver and gold with the cyanides of alkaline metals, are chiefly employed to yield the deposit of gold or silver.

On the large scale, metallic ores are reduced by a variety of processes, according to the nature of the metal and the composition of its ore. Oxides or carbonates, such as oxide of tin, and carbonates of iron, lead, copper, zinc, or cadmium, are simply heated with charcoal or coke, and in the case of zinc and cadmium, the reduced metal, being volatile at a strong red heat, is distilled off downwards, and collected in water. The other metals named are smelted along with a fusible mixture or flux—in the case of iron, a mixture of limestone and sandstone—which melts to a fluid glass, under which the melted metal collects, is protected from air, and may be drawn off by tapping the furnace below.

Where the ore is a sulphide, it is first roasted to expel the sulphur, and convert the metal into an oxide, which is then reduced as before. The roasting is performed by exposing the ore to the united action of a high temperature and of a current of air.

When the ore is much mixed with, or disseminated in stony or rocky matters, it is crushed to small fragments or to powder by machinery. The crushed mass is then exposed to a stream of water, when the denser portions, that is, the ore, is in a great measure separated from the lighter, and its bulk proportionately reduced.

Silver, which is often much disseminated, is extracted from the powdered mass by mercury, which dissolves it. The mercury is afterwards distilled off, and the silver left. Cinnabar, the bisulphide of mercury, is reduced by heating it with iron filings, which combine with the sulphur, and the metal is distilled from the sulphide of iron.

#### METALS WITH HYDROGEN.

Only a few metals unite with hydrogen, and some of these form gaseous and combustible compounds not yet known in a pure state, but only in a state of mixture with hydrogen gas. The following metals only are as yet known to combine with hydrogen:—zinc, copper, potassium, arsenic, antimony, and tellurium. Copper forms a solid hydride, which is deposited when hypophosphorous acid acts on sulphate of copper. It is a brown powder, suddenly decomposed by a heat of  $140^{\circ}$ .

## METALS WITH NITROGEN.

Until lately metals were not known to combine with this element: but we are now acquainted with compounds of nitrogen with copper, chromium, and mercury. These compounds are black or dark-brown powders, which may be obtained by passing dry ammoniacal gas over the oxides of the metals, gently heated, water being at the same time produced and nitrogen gas liberated. Thus, when oxide of copper is acted on by ammonia we have  $6\text{CuO} + 2\text{NH}_3 = 6\text{HO} + \text{NCu}_6 + \text{N}$ . Like the compounds of nitrogen with chlorine and iodine, these compounds are easily made to explode, their elements separating with violence, and with a flash of light, by a gentle heat, or friction, or percussion. It is possible, or indeed probable, that fulminating gold and silver, prepared by the action of ammonia on the oxides of these metals, and the explosive tendencies of which render them so very dangerous, are in reality the compounds of the metals with nitrogen. These must be distinguished from the other fulminating silver, which, like fulminating mercury, is a compound of oxide of the metal with fulminic acid.

## METALS AND CHLORINE.

The attraction or affinity between chlorine and metals is very strong. Many metals, such as potassium, copper, gold, antimony, &c., combine instantaneously with chlorine without the aid of heat, but with the phenomena of combustion. Others, such as mercury, &c., burn in chlorine only when they are heated in the gas, although mercury also rapidly combines with the gas, but without flame, when heat is not applied. By combining with chlorine, metals give rise to chlorides, which may be often more advantageously formed by other means than by direct combination with the gas. Other methods of obtaining chlorides are the following:—

1. Chlorine gas is passed over the oxide or sulphuret of the metal heated to redness. In many cases the affinity of chlorine prevails, and the oxygen or sulphur is expelled.  $\text{MO} + \text{Cl} = \text{MCl} + \text{O}$ . In the case of metals having a great affinity for oxygen, and forming volatile chlorides, such as aluminium, chlorine alone cannot decompose the oxide, but if the alumina be mixed with charcoal, and heated red-hot in a current of chlorine, the nascent metal combines with the gas, and sesquichloride of aluminium sublimes.  $\text{Al}_2\text{O}_3 + \text{C}_3 + \text{Cl}_3 = 3\text{CO} + \text{Al}_2\text{Cl}_3$ .



2. Hydrochloric acid gas is passed over the oxide or the sulphuret heated to low redness. Here the affinity of hydrogen for oxygen or sulphur, added to that of chlorine for the metal, effects decomposition which chlorine alone could not accomplish.  
 $MO + HCl = MCl + HO$  :  $MS + HCl = MCl + HS$ .

3. To the solution of an oxide, in water or in acids, hydrochloric acid or a soluble chloride is added. If the metal forms an insoluble chloride, that is at once precipitated, showing that change must be, as in the case of the dry gas,  $MO + HCl = MCl + HO$ . If the metal, as in the case of potassium, forms a soluble chloride, then the addition of hydrochloric acid causes no visible change: but on evaporation, crystals are deposited, which are generally found to be of chloride, and free from oxygen or hydrogen. Thus, potash, KO, with hydrochloric acid, HCl, undergoes, in solution, no change in appearance at first; but on evaporation yields cubical crystals, which are found to be KCl. Magnesia and alumina, when neutralised by hydrochloric acid, do not yield chlorides on evaporation. The chlorine is partly expelled, and oxide reproduced, and the dry mass is found still to contain hydrochloric acid.

4. Some metals, as gold and platinum, are converted into chlorides by dissolving them in aqua regia, or nitro-muriatic acid, and evaporating gently to dryness with an excess of hydrochloric acid. The dry residue is pure chloride.

When metals are combined with chlorine they may be reduced to the metallic state by various means.

1. Some chlorides are reduced by heat alone, which expels the chlorine. This is the case with almost all the chlorides of the noble metals.

2. Other chlorides are reduced by the action of another metal. Thus, chloride of platinum or chloride of silver is reduced by means of zinc.

3. Many chlorides are reduced by hydrogen gas at a red-heat, but not by charcoal, as oxides are.

4. The soluble chlorides of the noble metals are reduced by boiling their solutions with a formiate; those of gold and platinum, also, by the protosulphate of iron. Chlorides may be also reduced by fusion with the formiates or with cyanide of potassium.

5. Chloride of silver is often reduced by heating it with an alkaline carbonate, or with lime.

What has been said of the relation of metals to chlorine applies almost exactly to their relations with bromine, iodine, fluorine, and cyanogen, which, in its combination with

metals, plays the part of a salt radical, entirely analogous to chlorine.

The chlorides, bromides, iodides, and cyanides of metals are true salts, for the most part neutral salts. Indeed, sea-salt, the type of all salts, is chloride of sodium,  $\text{NaCl}$ . None of these compounds possess decided acid or basic characters ; but the chlorides, &c., are capable of combining together, and forming double chlorides, &c., which have been compared by Bonsdorff to oxygen salts. Thus viewing, as he did, chromate of potash,  $\text{KO}, \text{CrO}_3$ , as an oxygen salt, he viewed the following compound,  $\text{KCl}, \text{HgCl}_2$ , as a chlorine salt. The former contains, according to him, an oxygen acid,  $\text{CrO}_3$ , and an oxygen base,  $\text{KO}$  ; the latter, a chlorine acid (bichloride of mercury),  $\text{HgCl}_2$ , and a chlorine base,  $\text{KCl}$  (chloride of potassium). But it is to be observed that neither  $\text{KCl}$  nor  $\text{HgCl}_2$  have basic or acid properties ; they are, on the contrary, neutral salts, and, according to the more probable views now beginning to prevail as to the true nature of salts, which are considered compounds of metals with salt radicals, the compound  $\text{KCl} + \text{HgCl}_2$  is viewed as a double salt. The same view applies to a large number of analogous double chlorides, bromides, iodides, fluorides, and cyanides.

#### METALS WITH SULPHUR.

All the metals are capable of combining with sulphur, and many metallic sulphurets, or sulphides, as they are equally called, are found native : those of iron, copper, lead, antimony, zinc, and bismuth in abundance : those of mercury, silver, cadmium, and some others, more sparingly.

Most metals when heated along with sulphur combine with it ; but in many cases sulphurets are obtained by the action of sulphur compounds on the oxides, or by the deoxidation of sulphates.

1. When an oxide is exposed to the action of sulphuretted hydrogen gas, aided by heat, water and a sulphuret are formed,  $\text{MO} + \text{HS} = \text{HO} + \text{MS}$ . Or, with a sesquioxide,  $\text{M}_2\text{O}_3 + 3\text{HS} = 3\text{HO} + \text{M}_2\text{S}_3$ . The same change takes place when a solution of sulphuretted hydrogen or a current of the gas is made to act on solutions of oxides in acids. The sulphurets of the following metals may be thus obtained, being all insoluble in water :—

GROUP I. Metals, the oxides of which, in acid solutions, are precipitated as sulphurets by sulphuretted hydrogen.

| Metals.             | Colour of Precipitate. | Metals.                | Colour of Precipitate. |
|---------------------|------------------------|------------------------|------------------------|
| Cadmium . . . .     | Orange.                | Platinum . . . .       | Black.                 |
| Lead . . . . .      | Black.                 | Iridium . . . . .      | Black.                 |
| Bismuth . . . . .   | Black.                 | Gold . . . . .         | Black.                 |
| Copper . . . . .    | Black.                 | Tin, protoxide . . . . | Brown.                 |
| Silver . . . . .    | Black.                 | Tin, peroxide . . . .  | Yellow.                |
| Mercury . . . . .   | Black.                 | Antimony . . . . .     | Reddish orange.        |
| Palladium . . . . . | Black.                 | Molybdenum . . . . .   | Brown or red.          |
| Rhodium . . . . .   | Black.                 | Tungsten . . . . .     | Brown.                 |
| Osmium . . . . .    | Black.                 | Vanadium . . . . .     | Dark brown.            |
| Tellurium . . . . . | Yellow.                | Arsenic . . . . .      | Orange yellow.         |

The other metals are not precipitated by sulphuretted hydrogen, but the following yield sulphurets when their oxides in solution are acted on by hydrosulphuret of ammonia (sulphuret of ammonium), or by a soluble metallic sulphuret :—

GROUP II. Metals, the oxides of which are precipitated as sulphurets by soluble sulphurets, although not by sulphuretted hydrogen.

| Metals.           | Colour of Precipitate. | Metals.          | Colour of Precipitate. |
|-------------------|------------------------|------------------|------------------------|
| Iron . . . . .    | Black.                 | Cobalt . . . . . | Black.                 |
| Manganese . . . . | Flesh colour.          | Nickel . . . . . | Black.*                |
| Zinc . . . . .    | White.                 |                  |                        |

The remaining metals, those of the alkalies and earths, form a third group, the sulphurets of which being soluble do not appear as precipitates.

2. When a sulphate of a metallic oxide,  $\text{MO}$ ,  $\text{SO}_3$ , or  $\text{M}$ ,  $\text{SO}_4$ , is acted on by hydrogen or carbon at a strong red-heat, it is entirely deoxidised and the sulphuret of the metal is left. Thus, if sulphate of baryta,  $\text{BaO}$ ,  $\text{SO}_3$ , or  $\text{Ba}$ ,  $\text{SO}_4$ , be mixed with about one-sixth of its weight of charcoal, and exposed for two hours to a bright red-heat in a vessel closed, except where a small aperture is left for the escape of gaseous matter, carbonic oxide is given off and sulphuret of barium is left ;  $\text{BaO}$ ,  $\text{SO}_3 + \text{C}_4 = 4 \text{ CO} + \text{BaS}$ .

The sulphurets of each metal are commonly equal in number and analogous in composition to its oxides. Metallic sulphurets unite together, as oxides do, and produce double sulphurets or sulphur salts, which are closely analogous to oxygen salts.

Thus we have—

| Oxygen Salts.     |                |              |              | Sulphur Salts. |               |              |
|-------------------|----------------|--------------|--------------|----------------|---------------|--------------|
| Oxygen Acids.     |                | Oxygen Base. |              | Sulphur Acids. | Sulphur Base. |              |
| With Molybdenum . | $\text{MoO}_3$ | +            | $\text{KO}$  | $\text{MoS}_3$ | +             | $\text{KS}$  |
| With Arsenic .    | $\text{AsO}_3$ | +            | $\text{KO}$  | $\text{AsS}_3$ | +             | $\text{KS}$  |
| _____             | $\text{AsO}_5$ | +            | $3\text{KO}$ | $\text{AsS}_5$ | +             | $3\text{KS}$ |

Of course, if we view the oxygen salt,  $\text{AsO}_5$ ,  $3\text{KO}$ , for

\* Alumina is precipitated white by soluble sulphurets, but the precipitate is not sulphuret of the metal, but only hydrated oxide.

example, as a compound of a metal with a salt-radical,  $\text{AsO}_3$ ,  $\text{K}_3$ , the corresponding sulphur-salt  $\text{AsS}_3$ ,  $3\text{KS}$ , becomes  $\text{AsS}_3$ ,  $\text{K}_3$ . The analogy between the compounds of sulphur with metals, and those of oxygen with the same bodies, has been shown by Berzelius to be very complete.

Metallic sulphides are reduced to the metallic state in several ways.

1. The sulphide is heated to redness in a current of hydrogen, when hydrosulphuric acid is liberated, and the metal left.  $\text{MS} + \text{H} = \text{HS} + \text{M}$ ; or  $\text{M}_2\text{S}_3 + \text{H}_2 = 3\text{HS} + \text{M}_2$ .

2. The sulphide is heated with another metal; as, for example, bisulphide of mercury with iron.  $\text{HgS}_2 + \text{Fe}_2 = 2\text{FeS} + \text{Hg}$ . Tersulphide of antimony is also reduced when heated with iron.

3. The sulphide is heated with cyanide of potassium, as, for example, tersulphide of arsenic, which gives,  $\text{AsS}_3 + 3\text{KC}_y = 3\text{KS} + \text{Cy}_3 + \text{As}$ . Or the sulphide may be heated with formiate of soda, when sulphide of sodium is formed.  $\text{AsS}_3 + 3(\text{NaO}, \text{C}_2\text{HO}_3) = 3\text{NaS} + 3\text{CO} + 3\text{CO}_2 + 3\text{HO} + \text{As}$ .

4. The sulphide is heated with the carbonate of potash or soda, mixed with charcoal, or what is called black-flux. Such a flux is obtained by heating cream of tartar, or acid tartrate of potash, to redness in a covered crucible. The potassium seizes the sulphur, while the oxygen of the potash combines with the carbon, and the metal is reduced. Tersulphide of antimony may also be reduced in this way.

5. On the large scale, the most frequent method of reducing sulphides is to roast them in air, as already mentioned when speaking of the reduction of metals generally, and thus convert them partly or entirely into oxides. The roasted mass is then heated with charcoal, or charcoal and alkaline carbonate, and the metal thus obtained.

It has been already mentioned, that many negative sulphides combine with positive sulphides, forming sulphur salts, as sulphomolybdate of potassium,  $\text{KS}, \text{MoS}_3$ . Now these sulphur salts are usually soluble in water, and hence many insoluble sulphides dissolve in the soluble sulphides of potassium, sodium, ammonium, &c. This property is very useful in the analysis of metallic mixtures. The following table contains the names of the soluble sulphides which dissolve in sulphide of ammonium, or of potassium, and which may thus be separated from such as are insoluble in those sulphides.

Tersulphide of gold,  $\text{AuS}_3$ .  
 Bisulphide of platinum,  $\text{PtS}_2$ .  
 Sesquisulphide of rhodium,  $\text{Ro}_2\text{S}_3$ .  
 Tersulphide of arsenic,  $\text{AsS}_3$ .

Pentasilphide of arsenic,  $\text{AsS}_5$ .  
 Tersulphide of antimony,  $\text{SbS}_3$ .  
 Pentasilphide of antimony,  $\text{SbS}_5$ .  
 Bisulphide of vanadium,  $\text{VS}_2$ .

Tersulphide of vanadium,  $VS_3$ .  
 Tersulphide of tungsten,  $WS_3$ .  
 Tersulphide of molybdenum,  $MoS_3$ .  
 Quadrisulphide of molybdenum,  
 $MoS_4$ .

Protosulphide of tin,  $SnS$ .  
 Bisulphide of tin,  $SnS_2$ .  
 Bisulphide of tellurium,  $TeS_2$ .  
 Tersulphide of tellurium,  $TeS_3$ .  
 Various sulphides of iridium.

With selenium and tellurium metals form compounds very analogous to the sulphurets.

With phosphorus some metals combine and yield compounds called phosphurets, or phosphides, few of which are known. The alkaline phosphurets, as those of barium and calcium, yield by the action of water phosphuretted hydrogen gas, which takes fire spontaneously.

Metals combine in several cases with carbon, forming compounds which are called carburets, or carbides. They are generally brittle solids, and the only useful carburets are those of iron, which are two valuable compounds, steel and cast iron.

As all the compounds of metals with chlorine, bromine, iodine, fluorine, sulphur, and selenium, contain along with the metal a radical which forms an acid by combining with hydrogen, while the metal generally forms a base with oxygen, the question arises, what takes place when such metallic compounds are dissolved in water? Does the metal seize the oxygen, and the radical the hydrogen of an equivalent of water, and do the acid and base thus produced combine together?

In the case of an insoluble chloride, such as that of silver, we know that the hydrochloric acid does not combine with the oxide when both are mixed in solution, for the precipitate is found to be  $AgCl$ . Here the oxygen of the base and the hydrogen of the acid must have formed water :  $AgO + HCl = HO + AgCl$ .

But when hydrochloric acid,  $HCl$ , is mixed with potash,  $KO$ , or, what comes to the same thing, when chloride of potassium,  $KCl$ , is dissolved in water, what is the compound present in the liquid? Is it  $KCl$  simply dissolved as such? or, is it a salt,  $KO + HCl$ ? We know that the liquid, if evaporated, yields crystals of  $KCl$ , but it is possible that this compound may be formed by the force of cohesion, when it crystallises, and may not be previously present.

The general opinion of chemists is that in most cases soluble chlorides, sulphurets, &c., dissolve as such in water; but that in some cases, the hydrogen acid does appear to combine with the oxide.

If  $KCl$ , in dissolving, decomposes water, and forms  $KO + HCl$ , then we must admit that in the act of crystallising, when  $KCl$

separates, water is again recomposed. These continual decompositions and recompositions of water, without any visible change of properties, are so improbable that in most cases we cannot admit their occurrence.

But there are cases in which the solution of a chloride, &c., is attended with a change of properties. Thus, chloride of magnesium and chloride of aluminum, when dissolved in water, cannot again be obtained in the anhydrous form. On evaporation, oxide of magnesium or of aluminum are left, while hydrochloric acid escapes. Again, dry sesquichloride of chromium is peach-coloured, but its solution is deep green, the colour of all solutions containing sesquioxide of chromium; dry chloride of cobalt is blue, and its solution is pink, like all solutions containing oxide of cobalt.

In these and a few more similar cases, we can hardly doubt that water is decomposed when a chloride, &c., is dissolved; but in the great majority of cases we have no evidence of this; and therefore, it may be laid down as a general rule, that chlorides and analogous compounds dissolve as such in water, and that hydrogen acids mutually decompose metallic oxides, yielding water and compounds of the metal with the radical of the hydrogen acid. To this rule there are some exceptions; some chlorides, &c., in dissolving, decompose water, producing a hydrogen acid and an oxide; and hydrogen acids are capable of combining with some oxides without mutual decomposition, the compounds, however, not being very stable.

#### METALS WITH METALS.

Metals are capable of combining together, and forming compounds which retain the metallic character, and many of which are highly useful. They are called alloys, except where mercury is one of the metals, when they receive the name of amalgams. Thus, brass is an alloy of copper and zinc; pewter an alloy of lead and tin; German silver an alloy of copper, zinc, and nickel. The metal used for silvering the backs of mirrors is an amalgam of tin and lead; that is, it contains mercury with these metals. The alloys will be briefly described hereafter.

The progress of modern chemistry has added largely to the number of the elementary metals. Before the middle of last century the metals known were only such as had long been used in the arts or in medicine, and did not exceed twelve in number. From that period many new metals were gradually discovered in the mineral kingdom; and, in 1807, Davy's discovery of the metals of the alkalis at once added a numerous

class of metals to the list. Wollaston and Smithson Tennant had previously, in 1803, discovered the four remarkable metals, associated with platinum in its ores. The whole number of ascertained metals is now forty-two; and, some few years ago, Mosander announced the discovery of three new metals, accompanying cerium and yttrium; Rose that of two, associated with columbium; and Klaus that of one more in the ore of platinum. These, and one or two others, still more recently announced, if established, will raise the number to fifty.

In considering the metals individually, we shall arrange them in groups or classes, according to their affinities for oxygen and to their chemical relations.

CLASS I. includes twelve metals, besides ammonium, subdivided into three well-marked orders.

*Order 1.* Metals of the alkalies proper, namely—

|            |         |          |           |
|------------|---------|----------|-----------|
| Potassium. | Sodium. | Lithium. | Ammonium? |
|------------|---------|----------|-----------|

These metals have so strong an affinity for oxygen that they are rapidly oxidised by exposure to the air, and decompose water with violence, disengaging hydrogen gas, which generally takes fire. Their oxides are powerful bases or alkalies, very soluble in water and very caustic. Ammonium is here added, because although it is a compound body, and not yet known in the uncombined state, it is closely analogous to potassium, and indeed is isomorphous with it. Moreover its salts are perfectly analogous to those of potassium.

*Order 2.* Metals of the alkaline earths, namely—

|         |            |          |            |
|---------|------------|----------|------------|
| Barium. | Strontium. | Calcium. | Magnesium. |
|---------|------------|----------|------------|

These metals have also a very strong affinity for oxygen, and, except magnesium, they decompose water at ordinary temperatures, but without flame. Their oxides are powerful bases, but less soluble and caustic than the alkalies; indeed, oxide of magnesium is insoluble. As they are thus intermediate between the alkalies and the earths proper, they are called alkaline earths.

*Order 3.* Metals of the earths proper, namely—

|           |            |          |
|-----------|------------|----------|
| Aluminum. | Glucinum.  | Yttrium. |
| Thorium.  | Zirconium. |          |

These metals do not decompose water at ordinary temperatures, but burn in air when heated, forming oxides, which are less powerful bases than the preceding; and being quite insoluble in water and earthy in aspect, they are called the earths.

Some of the new metals, as yet little known, belong to this group.

CLASS II. includes thirty metals ; which are also subdivided into three orders. All these metals combine with oxygen, and in general their protoxides are insoluble and of an earthy aspect, but coloured, and have basic characters, in many cases very powerful. A considerable number of these metals form acids with a larger proportion of oxygen. This class contains all the heavy metals, and all those which, from their malleability, ductility, &c., have long been used by mankind.

*Order 1.* Metals, the protoxides of which are powerful bases, but which do not decompose water unless with the aid of a red-heat : namely—

|            |          |         |
|------------|----------|---------|
| Manganese. | Tin.     | Cobalt. |
| Zinc.      | Cadmium. | Nickel. |
| Iron.      |          |         |

*Order 2.* Metals which do not decompose water at any temperature ; but the oxides of which, once formed, cannot be reduced by heat alone : namely—

|             |              |            |
|-------------|--------------|------------|
| Arsenic.    | Columbium.   | Bismuth.   |
| Chromium.   | Antimony.    | Titanium.  |
| Vanadium.   | Uranium.     | Tellurium. |
| Molybdenum. | Cerium ?     | Copper.    |
| Tungsten.   | Lanthanium ? | Lead.      |

It is doubtful whether cerium and lanthanum do not belong to the preceding order, to which also belong, possibly, the three new metals of Mosander, didymium, erbium, and terbium. Ilmenium, a supposed new metal, found with columbium, most probably belongs to Order 2.

*Order 3.* Metals, the affinity of which for oxygen is so feeble that their oxides are reduced by a red-heat : namely—

|          |            |            |
|----------|------------|------------|
| Mercury. | Platinum.  | Osmium.    |
| Silver.  | Palladium. | Iridium.   |
| Gold.    | Rhodium.   | Ruthenium. |

Owing to the comparatively feeble affinity for oxygen of these metals, they have no tendency to rust when exposed to the air, as iron does, for example, from its strong attraction for oxygen. Hence they retain the brilliant lustre of their polished surface, and do not wear by exposure to the air. They are therefore often called the noble or precious metals.

We now proceed to the description of the separate metals, which may be made very brief in consequence of our having so minutely described the general chemical characters of metallic



bodies, the analogy among which is so great that the description of one is applicable, with but little change, to the others.

## METALS.—CLASS I.

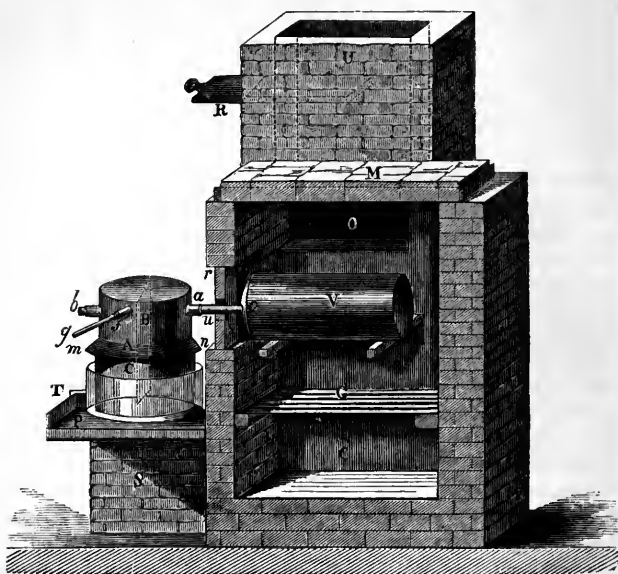
### ORDER 1.—METALS OF THE ALKALIES PROPER.

#### 14. POTASSIUM. $K = 39.2$ .

SYN. *Kalium*.—This metal occurs chiefly in the ashes of land-plants, as oxide, or potash united to carbonic acid; it is also found as chloride in the ashes of sea-plants. Many abundant rocks, such as felspar (with all its derivatives, including the clays), and mica, besides many simple minerals, contain potassium in considerable quantity. It is contained also in most fertile soils, being necessary to the growth of plants, in the form of potash. Potassium was discovered in 1807, by Davy, who obtained it by the action of a powerful galvanic battery on hydrate of potash,  $KO,HO$ . At the negative pole oxygen was given off, and at the positive pole appeared hydrogen, derived from the water of the hydrate, along with the globules of a metal resembling mercury, which took fire in the air and burnt, reproducing potash. This expensive and troublesome method has long been abandoned, and potassium is now prepared by the action of charcoal, at a white-heat, on carbonate of potash,  $KO, CO_2$ .

A mixture of carbonate of potash with finely divided charcoal is first prepared by igniting cream of tartar in a covered crucible, which leaves such a mixture, well known as the black flux. This, while still warm, is mixed with a considerable proportion of charcoal in coarse powder and small fragments recently ignited and allowed to cool in a covered crucible. The whole is now introduced into one of the hammered iron bottles used for holding mercury, coated outside with a mixture of sand and clay. The bottle is placed horizontally in a wind furnace (see figure), and a short wide tube of iron is fitted to it, to which tube is attached a copper receiver, partly filled with good naphtha, and having a diaphragm of copper, and on the further side of the receiver an aperture for the escape of gas, opposite the tube of the bottle: so that, if necessary, a strong steel rod may be introduced through this aperture, and another in the upper part of the diaphragm into the tube, for the purpose of cleaning it out, as it is apt to become choked. The receiver with the naphtha being surrounded with ice, a steady and uniform

strong red or white-heat (by means of dry wood, the flame of which plays all round the bottle), is applied to the bottle,



and after a time potassium, which is known by the appearance of its pink flame at the mouth of the tube, distils over, accompanied with carbonic oxide gas, and with a gray powder, which is the cause of the occasional choking of the tube. The potassium drops into the naphtha, which protects it from the action of the air. To purify it entirely, it is redistilled in a small iron retort along with a little naphtha into a receiver containing that liquid.

In this process the carbon deprives the oxide of potassium and the carbonic acid of their oxygen, forming carbonic oxide gas.  $\text{KO}, \text{CO}_2 + \text{C}_2 = \text{K} + 3\text{CO}$ . Were this all, we should have no other product but potassium and carbonic oxide. Unfortunately, however, carbonic oxide at a red-heat enters into combination with potassium, forming the gray powder above mentioned; the composition of which is  $7\text{CO} + \text{K}_3 = \text{C}_7\text{O}_7, \text{K}_3$ . If, therefore, we consider the products obtained from 4 eqs. of carbonate of potash, they ought to be as follows, if the gray compound were not formed,  $4(\text{KO}, \text{CO}_2) + \text{C}_3 = \text{K}_4 + 12\text{CO}$ .

Instead of obtaining 4 eqs. of potassium, however, from 4 eqs. of carbonate, we only obtain 1 eq. as metal, the remaining 3 eqs. combining with carbonic oxide to form the gray powder.  $K_4 + 12CO = (C_7O_7, K_3) + 5CO + K$ . This is the reason why the above process is not nearly so productive as might be expected. The gray powder must be kept under naphtha, as it is liable to be altered if exposed to the air, and especially to take fire and explode, if moistened with water. (This compound, by the slow action of the air, is converted into a very remarkable salt, rhodizionate of potash, to be hereafter mentioned, when carbonic oxide is treated of as a compound radical). By an improvement in the form of the receiver, which is now made of strong iron plates, and very broad and shallow, the metal is more quickly cooled, as well as the carbonic oxide, so that much less of the gray powder is formed. By this means the loss of potassium has been reduced to from  $\frac{1}{4}$  to  $\frac{1}{3}$  of the quantity present.

Potassium is a metal of a bluish-white colour, and a high degree of metallic lustre, so that a melted portion of it under naphtha, resembles mercury or melted silver. At ordinary temperatures, it is so soft as to yield easily to the finger. At  $150^\circ$  it is quite fluid, and if cooled to  $32^\circ$ , it becomes brittle. At a low red-heat it boils, and may be distilled unchanged. Its vapour is green. The Sp. G. of the metal is 0.865, so that it floats on the surface of water.

When exposed to the air it is instantly tarnished by the formation of a film of oxide; and after a short time the whole is oxidised and converted into a white solid oxide, which soon attracts water from the atmosphere. Potassium must therefore be kept under naphtha, a liquid containing no oxygen. When heated in the air, potassium takes fire, and burns with a beautiful pink flame, oxide being formed. So powerful is its affinity for oxygen, that when thrown on the surface of water, it instantly decomposes it, with so much disengagement of heat as to set fire to the hydrogen gas which is separated.  $K + HO = KO + H$ . The hydrogen burning causes the potassium also to burn, combining with the oxygen of the air, and the globule swims about until it is consumed, burning on the surface of the water with a beautiful pink flame. The same phenomenon appears if the metal be placed in a small hollow on the surface of a piece of ice, when it instantly bursts into flame.

When a globule of potassium burns in water, there is always observed just before it disappears, and when it has lost the metallic appearance, a sharp explosion; which is not quite with-

out danger, as it scatters about particles of fused caustic potash, one of which may enter the eye of the operator. This explosion depends on a very curious and interesting circumstance : namely, that the melted globule only comes into contact with the water when it has cooled to a certain point, when it is, however, hot enough to convert into steam a considerable amount of water.

This phenomenon has recently been investigated in its general form by Boutigny, who has obtained very interesting results. These, although belonging strictly to physics, may here be briefly noticed.

If, as first observed by Leidenfrost, we heat a capsule of platinum a little beyond  $212^{\circ}$ , and drop water into it, the water is rapidly boiled off. But if we heat the capsule red-hot, we may then drop into it gradually as much water as will nearly fill it, while the vessel continues red-hot, and the water not only does not boil, but is not hot enough to scald the finger. If we examine the drop or mass of water, it will be seen to be in a kind of gliding motion, moving over the surface of the metal, and evidently not touching it. If now we remove the heat, as soon as the capsule cools down so far as that the drop comes in contact with it, it is rapidly boiled away, almost with explosion, the metal being still heated considerably beyond  $212^{\circ}$ .

The true explanation seems to be this ; that each liquid possesses, at a certain temperature, so much repulsion for the particles of a given solid, such as a metal, as not to come into what is called contact with it, but to roll about freely over its surface. This is the case with mercury when placed on wood, glass, or iron, at the ordinary temperature ; when it forms globular drops, like those of water in the red-hot capsule. But there are some metals, such as tin, on which mercury spreads as water does ; in other words, in which it moistens the surface. Now, water moistens all metals at the ordinary temperature, but not at a red-heat, when it assumes the spherical or spheroidal state of mercury at the ordinary temperatures. It is obvious, that the moistening of a solid with any liquid is due to chemical attraction between the particles of the two bodies, and that when the solid is heated far beyond the liquid, which cannot be heated beyond its boiling point, the repulsion, caused by heat, at a certain point overpowers that attraction, and the solid is no longer moistened, that is, ordinary contact no longer exists. In these circumstances heat passes with extreme slowness from the solid to the liquid, chiefly by radiation, and the evaporation assists in keeping down the temperature of the latter.

Hence we may safely immerse the finger in water contained in a red-hot vessel, as the water never reaches its boiling-point

until the vessel is far below a red-heat, and contact is again re-established. On the same principle is explained the apparent paradox, that we can plunge the hand into *red-hot* melted lead or iron without danger, but are fearfully burned *if the metal be not sufficiently hot*, because in the former case, the moisture of the hand does not come in contact with the metal, but in the latter it does. Hence the long discredited statements, that men employed in smelting furnaces were in the habit of dipping their hands in the metal as it flowed from the furnace, are now fully confirmed and explained, and any one may repeat, as I have often done, the apparently dangerous experiment. Again, the trick of passing a bar of red-hot iron across the tongue; and the successful trial of the ordeal of walking on red-hot ploughshares, not unfrequent in the middle ages, are only modifications of the above experiment.

Boutigny has shown that not only water, but far more volatile liquids may be kept in the liquid (and spheroidal) state in red-hot metal. Thus, liquid sulphurous acid, which boils at  $14^{\circ}$ , may be dropped into the red-hot capsule, and will there evaporate, but not boil; and by its evaporation will produce so intense a cold in the middle of the red-hot vessel, that if some water be now dropped into it, the water is instantly frozen, and may be turned out as a mass of ice, while the vessel continues at a red or even a white-heat.

When the laundress drops a little saliva on her smoothing-iron, and the liquid rolls off without moistening the metal, she judges of the temperature of the iron on the same principle. If it be too cold, or rather not hot enough, the saliva adheres to it and boils off.

To return to the globule of potassium. As long as the metal burns, it is too hot to come in contact with, or be moistened by, the water, and it rolls about exactly like mercury on iron. But when all is burned, and only the melted oxide is left, it continues to roll about, till it cools down sufficiently to permit contact, when it is still so hot as instantly to convert some water into steam, and thus cause the explosion.

The affinity of potassium for oxygen and the other metalloids is so powerful that it has been the means of isolating many metals and some metalloids, whose attraction for oxygen, &c., is too strong to be overcome by the usual means. Thus potassium decomposes the oxides or chlorides of aluminum, glucinum, yttrium, thorium, and zirconium, and the boracic and silicic acids. It is, consequently, a very powerful instrument of research.

The compounds of potassium to be here described are those which it forms with the metalloids.

## POTASSIUM AND OXYGEN.

Potassium forms two compounds with oxygen, a protoxide KO, and a peroxide  $\text{KO}_2$ .

a. Protoxide of Potassium.  $\text{KO} = 47.2$ .

This oxide is only formed when potassium is oxidised in pure dry air, or oxygen. It is a white powder, which rapidly absorbs moisture from the air, and deliquesces. It is then converted into the usual form, namely, hydrated oxide of potassium, or hydrate of potash.

*SYN. Caustic Potash.*  $\text{KO}, \text{HO} = 56.2$ .—This important compound is best prepared by acting on pure carbonate of potash, dissolved in water, so as to deprive it of carbonic acid. Two parts of carbonate are dissolved in twenty of boiling water in an iron pot, and one part of quick lime, being previously slaked by covering it with boiling water, so as to form a kind of cream of slaked lime, is added to the boiling liquid in small portions, the mixture being allowed to boil a minute or two after each addition. When all the lime has been added, the whole is to be boiled for five minutes, care being taken to keep up the original quantity of water; since with less water, the potash actually takes back the carbonic acid from the lime. The vessel, which ought to be more deep than wide, is then covered up with its lid, and allowed to stand for 24 hours. At the end of that time, if the above directions have been exactly followed,  $\frac{19}{20}$  of the liquid may be decanted off perfectly clear and colourless. This is a pure solution of potash, and to obtain the hydrate, we have merely to boil it rapidly down, in a clean deep iron or silver vessel, till the residue flows like oil. It is then poured out on a plate of silver, and, on cooling, broken up into fragments, and preserved in well stopped bottles.

In the above process, the lime deprives the carbonate of potash of its carbonic acid, forming an insoluble carbonate of lime.  $\text{KO}, \text{CO}_2 + \text{CaO}, \text{HO} = \text{CaO}, \text{CO}_2 + \text{KO}, \text{HO}$ . By slaking the lime with hot water, it falls to so fine a powder that every particle acts, and we are thus enabled to use very little more than the atomic proportion of quick-lime, which would be about 28 to 69, instead of 1 to 2, or 28 to 56, as we employ. Again, by adding the lime gradually, and constantly boiling, the carbonate of lime assumes a very dense form, and settles perfectly to the bottom; whereas, if the lime were all added at once it would yield a very bulky carbonate from which the solution of potash would be with difficulty separated. By allowing the liquid to

clear in the covered vessel, we avoid filtration and, consequently, the bringing the potash in contact with the air, from which it absorbs carbonic acid, and is reconverted into carbonate. So effectual is the above process, that the decanted liquid does not effervesce with acids, if carefully prepared ; and if it be rapidly boiled to dryness, the solid hydrate may be also obtained free from carbonic acid.

The hydrate of potash is so valuable a re-agent to the chemist, that I have described minutely the best method of preparing it, which, as generally happens, is also the most simple. The solution, or aqua potassæ, is daily used in the ultimate analysis of organic bodies, to absorb carbonic acid ; and for this purpose, as well as for many others, it is obtained sufficiently pure from the pearlash, or impure carbonate of potash of commerce. The pearlash is to be treated precisely as the pure carbonate in the above process ; and the decanted solution of caustic potash is to be boiled down until crystals begin to form in the boiling liquid, which is then allowed to cool in well stopped bottles of green glass. The crystals are sulphate of potash, a salt present in the pearlash, which is insoluble in a strong solution of caustic potash. On cooling, therefore, the whole of the sulphate crystallises out, so that not a trace is left in the liquid. The clear liquid, decanted from the crystals, now contains no impurity, except chloride of potassium, which, for most purposes, is of no importance. It has a Sp. G. of 1·25 to 1·35, and is ready for use in organic analysis. If boiled to dryness, it yields a hydrate of potash, far purer than the hydrate of commerce, inasmuch as it is free from sulphate.

Hydrate of potash is best obtained by boiling down the pure solution in a deep silver vessel till it flows like oil. It is then the monohydrate, and when cast in small sticks, is much used by surgeons as a powerful caustic. The chief objection to its use is, that owing to its attraction for water, it deliquesces, and spreads farther than is intended. But in careful hands, it is easily managed, and is often used in preference to the knife, for opening glandular swellings, such as buboes, which have suppurated. When thus opened, and when the caustic has been applied to the inner surface of the cavity, they appear to heal better than when opened with the lancet. By smearing with oil the parts surrounding that to be cauterised, the spreading of the caustic potash is prevented. In chemistry hydrate of potash is much used for the decomposition of minerals, by fusion with them, and for drying certain gases. It acts so strongly, at a red heat, on all substances containing silica, that it is apt to corrode the vessels, crucibles, &c., in which it may be heated ; and it even corrodes platinum when ignited in it,

the metal being oxidised. Gold and silver are less acted on by it, but it oxidises many other metals, as well as boron and silicon, when heated with them, air being admitted.

The solution of potash, *aqua potassæ*, or *liquor potassæ*, has the acrid corrosive taste of the hydrate; and when rubbed between the fingers, gives them a soapy feel, forming, in fact, soap with the oil of the skin. It turns infusion of red cabbage, of violets, dahlias, &c., green, and restores the blue of litmus reddened by acids. It is powerfully alkaline, or basic, neutralising all acids. Its great attraction for carbonic acid has been already mentioned as the reason of its being used in organic analysis, for the purpose of absorbing the carbonic acid derived from the carbon of the substance, and enabling us to ascertain its weight. For this purpose, the solution must have a density of at least 1.25. From its affinity both for water and for carbonic acid, potash in the form of solid hydrate, or in solution, must always be protected from the atmosphere. The solution, when of Sp. G. 1.060, is used in medicine as an antacid and lithontriptic. The chief use of potash is unquestionably that of promoting the growth of plants, to which it is generally essential, although it may frequently be replaced by soda or lime. Its function appears to be that of fixing the carbonic acid of the atmosphere, which, with the elements of water, gives rise to the chief vegetable products, as will be explained in the second part. Hence, all fertile soils contain it; hence also the value of the ashes of vegetables, as manure, depends, in a great measure, on the potash they contain; and the same remark applies to animal manures. Cow-dung, for example, is very rich in potash.

Potash is extensively used in various arts and manufactures, as in glass-making, glass being an acid silicate of potash (or soda) and lime; in soap-making, in bleaching, &c. Salts of potash are used to supply that base in the manufacture of alum and of nitre, on the latter of which depends that of gunpowder.

The presence of potash in any solution is best ascertained by the action of bichloride of platinum in solution, which, if any notable quantity of potash be present, forms with it a pale yellow precipitate of the double chloride of platinum and potassium. If the proportion of potash be very small, no precipitate may appear; in this case the liquid to be tested may be first concentrated by evaporation, and then again tested with the platinum salt, when the precipitate will in all probability appear; or alcohol may be added to the first mixture, in which the double chloride is quite insoluble. The only uncertainty in this test is, that ammonia gives a similar precipitate; so that we must first



ascertain if ammonia be present ; and if so, expel it by a red-heat, before testing for potassium.

Perchloric acid also causes in solutions containing potash a white precipitate of perchlorate of potash, sparingly soluble in water, and quite insoluble in alcohol, so that if but little potash be present, alcohol ought here also to be added.

An excess of tartaric acid produces, after a time, a crystalline deposit of cream of tartar, in solutions containing potash, more especially if well stirred with a glass rod, which causes the deposit to appear in streaks on the glass.

An alcoholic solution of carbazotic acid causes a yellow crystalline precipitate in solution of potash.

Lastly, hydrofluosilicic acid causes a gelatinous semi-transparent precipitate of silicofluoride of potassium, when added to solutions of potash : of all these tests, the most certain is the bichloride of platinum, with the aid of alcohol, by means of which potash may be both separated from soda, and its quantity accurately determined.

b. Peroxide of Potassium.  $KO_2 = 63.2$ .

This oxide is formed by passing oxygen over red-hot potash. It is an orange-yellow powder, forming when fused, a crystalline mass on cooling, which, when thrown into water, is decomposed, oxygen being given off, and potash being found in the liquid.

POTASSIUM WITH HYDROGEN AND NITROGEN.

With hydrogen, potassium forms two compounds, one of which appears to be a solid, the other a gas. The latter seems to take fire spontaneously in contact with air, and is probably formed when potassium acts on water. The former is produced when potassium is heated in hydrogen gas. It is a gray solid decomposed by water.

When potassium is heated in dry ammonia, an olive-coloured solid is formed, which may be viewed as ammonia in which 1 eq. of hydrogen has been replaced by potassium,  $NH_2K$ . When this is heated, ammonia is given off, and there is left a substance resembling graphite, which is a compound of potassium and nitrogen ; ammonia, in fact, in which all the hydrogen has been replaced by potassium ;  $3NH_2K = 2NH_3 + NK_3$ . This compound has been little examined.

POTASSIUM WITH CHLORINE, BROMINE, IODINE, AND FLUORINE.

With all these elements potassium combines, with each in one proportion only, forming compounds which are very analogous to each other.

Chloride of Potassium.  $KCl = 74.7$ .

This compound is a neutral salt, very similar to sea-salt. It is found in considerable quantity in the ashes of plants, especially of sea-plants. It is formed when potash is neutralised by hydrochloric acid, and the solution evaporated so as to form crystals.  $KO + HCl = HO + KCl$ . It is also left when chlorate or perchlorate of potash is heated so as to expel all the oxygen.  $KO, ClO_3 = KCl + O_2$ .

It has a saline and bitterish taste, and is not much more soluble in hot than in cold water. It crystallises, like sea-salt, in cubes. With bichloride of platinum it forms a pale yellow sparingly soluble double salt,  $KCl, PtCl_2$ . Similar compositions are formed with the bichlorides of palladium and iridium, the sesquichloride of rhodium, &c., and with the terchloride of gold. Chloride of potassium is only used, when very cheap, in the manufacture of alum. It cannot be substituted for sea-salt, as a condiment, or antiseptic.

Iodide of Potassium.  $KI = 166.3$ .

This salt, which is very much used in medicine, and in the arts, especially that of photography, resembles the preceding in external character. It crystallises in cubes, and is very soluble in water. To prepare it, iodine is dissolved in a pure solution of potash, with the aid of heat, until the liquid begins to assume a permanent brownish-yellow colour, indicating a slight excess of iodine. The liquid is now evaporated to dryness, and the dry residue ignited and melted in a covered platinum or iron vessel. The melted mass is poured out on a clean iron plate. It is iodide of potassium; and if dissolved in water and filtered, if necessary, the solution on evaporation yields pure crystals of the salt. In the first stage of this process, iodate of potash and iodide of potassium are formed:  $I_2 + 6KO = 5KI + (KO, IO_3)$ . In the second stage, the iodate is converted, by a red-heat, into iodide of potassium, oxygen being given off, while the iodide already present is unaltered:  $5KI + (KO, IO_3) = 6KI + O_2$ .

Another method is to form iodide of iron by bringing iron and iodine in contact under water. The iodide of iron dissolves, and the filtered solution is decomposed, at the boiling temperature, by an equivalent weight of carbonate of potash in solution; the solution of the carbonate being added in successive small portions.  $FeI + KO, CO_2 = KI + FeO, CO_2$ . The insoluble carbonate of iron is separated by the filter, and the clear liquid evaporated till crystals are deposited.

Pure iodide of potassium is white, and dissolves entirely in

hot alcohol. It is often adulterated with carbonate of potash, but that salt is easily detected by its insolubility in alcohol. The solution of iodine of potassium can dissolve a large quantity of free iodine, by which it acquires a deep brown colour. This solution is much used for baths ; and the iodide is employed both externally and internally in scrofulous diseases.

Bromide of Potassium.  $KBr = 119\cdot2$ .

This salt is very analogous to the preceding, and is formed in the same way. It crystallises in cubes, and is very soluble in water. It has not been applied to any use.

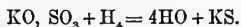
Fluoride of potassium,  $KF = 58\cdot1$ , is obtained when hydrofluoric acid acts on potash.  $HF + KO = HO + KF$ . It is soluble and crystallises in cubes, and is very analogous to the preceding salts.

#### POTASSIUM AND SULPHUR.

Potassium combines with sulphur in several proportions, of which the most important are the protosulphuret,  $KS$ , and the pentasulphuret, or persulphuret,  $KS_5$ .

Protosulphuret of Potassium.  $KS = 55\cdot2$ .

This may be formed by melting together its constituents ; but it is best prepared by passing hydrogen gas over neutral sulphate of potash, heated to bright redness. Here the hydrogen removes all the oxygen of the salt, and the sulphuret is left.



Protosulphuret of potassium is a solid of a bright red colour, which forms with water a colourless solution. This solution smells of sulphuretted hydrogen, and probably contains that compound and potash, formed by the action of water on the sulphuret.  $KS + HO = KO + HS$ . The solution is alkaline, and if pure is decomposed by acids, without any separation of sulphur, sulphuretted hydrogen being given off.

Pentasulphuret or Persulphuret of Potassium.  $KS_5 = 119\cdot2$ .

This is the chief ingredient in what is called hepar sulphuris, or liver of sulphur, when prepared by fusing sulphur with carbonate of potash at the lowest possible temperature, when the persulphuret is formed along with hyposulphite of potash :  $3 KO + S_{12} = 2 KS_5 + (KO, S_2 O_2)$ . Alcohol dissolves the sulphuret, which has a deep orange colour. It may be obtained pure in solution by boiling the protosulphuret with 4 eqs. of

sulphur and water. The persulphuret of potassium forms an orange or yellow solution, which is decomposed by acids, with the deposition of a large quantity, 4 eqs. of sulphur.

There are 5 other compounds of sulphur and potassium, all similar in properties to the persulphuret. They are  $\text{KS}_2$ ,  $\text{KS}_3$ ,  $\text{KS}_4$ ,  $\text{K}_2\text{S}_7$ , and  $\text{K}_2\text{S}_9$ . The last two are probably  $(\text{KS}_2 + \text{KS}_6)$  and  $(\text{KS}_4 + \text{KS}_5)$ .

#### POTASSIUM AND SELENIUM.

The relations between these elements appear to be closely analogous to those between potassium and sulphur, but the compounds formed are little known.

#### POTASSIUM AND PHOSPHORUS.

These elements, when heated together, combine to form a solid phosphuret. When thrown into water, it gives rise to the disengagement of spontaneously inflammable phosphuretted hydrogen, while solid phosphuretted hydrogen separates, and hypophosphite of potash is found dissolved.

Nothing is known with certainty of the carburet of potassium, which is supposed by some to be formed in the process of making potassium.

No compound of potassium with silicon is accurately known ; but with silicic acid potash forms compounds, which are known as glass. When the silica predominates, we have ordinary hard insoluble glass, which, however, in practice, contains lime, and in the case of green glass, protoxide of iron ; flint glass contains also oxide of lead. When the potash is in excess, the compound is called silicate of potash. It is a glassy mass, soluble in water, and the solution has long been known as liquor of flints.

#### 15. SODIUM. $\text{Na} = 23$ .

*SYN. Natrium.*—This metal is, perhaps, more abundant in our globe than any other, except, perhaps, aluminium ; for it constitutes two-fifths of all the sea-salt existing in sea-water, in the water of springs, rivers, and lakes, in almost all soils, and in the form of rock-salt. Sea-salt is a compound of sodium with chlorine,  $\text{NaCl}$ . Sodium also occurs as oxide of sodium, or soda, in a good many minerals : and more especially in the forms of carbonate, nitrate, and borate of soda : the first extracted from the soil in many parts of Africa ; the second covering extensive plains in South America ; and the third encrusting the shores of numerous lakes in Thibet. Soda is contained in sea-plants,

and in land-plants growing near the sea, in the latter apparently replacing potash ; it is the chief base in kelp, varec, or barilla, which are the ashes of sea-weed. Soda also occurs in most animal fluids.

Sodium is obtained by a process exactly similar to that above described for potassium, substituting acetate of soda for cream of tartar. Owing to the fortunate circumstance that sodium does not combine with carbonic oxide, the process is much more productive than in the case of the former metal. In fact, when properly conducted, we may expect to obtain the whole of the sodium. Thus, in the laboratory at Giessen, 1 lb. of calcined acetate of soda (carbonate containing a little charcoal) mixed with  $\frac{1}{4}$  lb. of finely-powdered, and  $\frac{1}{2}$  lb. of coarsely-powdered charcoal, and heated in a malleable iron bottle, as above recommended, yielded nearly 5 oz. of sodium, even when it was obvious that the result was capable of considerable improvement; the whole of the sodium present being about 7 oz. From the extreme cheapness of carbonate of soda, and the productiveness of the operation, sodium can be prepared far cheaper than potassium, and may, in most cases, be substituted for that metal, as its affinities are almost equally powerful. Should this metal be ever required on the large scale, it might be obtained for a price little, if at all, higher than that of zinc.

Sodium is a silver-white metal, having a very high lustre. It has not the bluish tinge of potassium, but if any, rather a very slight yellowish tint, so that it resembles silver, while potassium resembles mercury. Its Sp. G. is 0.9348 ; it melts at  $200^{\circ}$ , being rather less fusible than potassium, melting at  $194^{\circ}$  ; but it is, on the other hand, somewhat more volatile, which is one cause of its preparation being easier, since it distils over at a lower heat.

#### SODIUM AND OXYGEN.

The affinity of sodium for oxygen is next to that of potassium. It rapidly attracts oxygen from the air, and must therefore be kept under naphtha ; but it is evidently less rapidly oxidised than potassium, and consequently keeps better. When heated in air or oxygen it takes fire, burning with a very pure and intense yellow flame, which is characteristic of sodium and of all its compounds. It decomposes water instantly, but does not spontaneously take fire when thrown on water, as potassium does. If the water, however, be thickened with gum, or if there be only a few drops of water, the action of sodium is attended with flame, and the yellow colour of the flame is most conspicuous.

When exposed to the air, or burned in air or on water, sodium forms the protoxide, or soda : but it can form two other oxides—the suboxide and the peroxide. The suboxide is little known ; the peroxide is an orange powder, said by some to be  $\text{NaO}_2$ , by others  $\text{Na}_2\text{O}_3$ , by others again  $\text{NaO}_3$ . The only important oxide is the

Protoxide of Sodium.  $\text{NaO} = 31$ .

*SYN. Soda.*—This oxide is formed when sodium is burned in dry air or oxygen. It is a white powder which attracts moisture and carbonic acid from the air. When sodium is oxidised by water, or when the protoxide is dissolved in water, there is formed the true alkali, the hydrated oxide of sodium, or hydrate of soda,  $\text{NaO}, \text{HO}$ .

*SYN. Caustic Soda.*—This hydrate is prepared by a process exactly similar to that given for caustic potash, substituting carbonate of soda for carbonate of potash. If the carbonate of soda be in crystals, 1 part of quick lime is sufficient for 5 or 6 parts of carbonate : if dry, 1 part of quick lime will suffice, if pure, for 2 of carbonate. As the lime is seldom pure, it is in general safer to take 2 parts for 3 of dry carbonate of soda.

The solution of caustic soda, owing to the superior purity of the carbonate, which is generally free from sulphate and chloride, is much purer than the common aqua potassæ : and when boiled down it leaves a very pure hydrate of soda,  $\text{NaO}, \text{HO}$ . This hydrate is in all external characters, and in most chemical ones, exactly similar to caustic potash : it is deliquescent and caustic, and may be used for almost all the same purposes. The solution, however, cannot be used for organic analysis, as it froths up like solution of soap when a gas passes through it.

With acids soda forms salts, all of which, with hardly an exception, are soluble in water, and many of which crystallise. The solubility of its salts serves to distinguish soda from potash, for neither bichloride of platinum, tartaric acid, perchloric acid, nor carbazotic acid causes any precipitate in the salts of soda, even when alcohol is added. Hydrofluosilicic acid is the only test that forms a precipitate in cold and pretty strong solutions of soda salts ; but the silicofluoride of sodium, thus formed, is more soluble than the corresponding salt of potassium. When we know that either potash or soda is present, and the tests give the above negative results, we may safely decide on the presence of soda ; but if we wish for positive evidence, this can only be obtained by setting fire to alcohol along with the suspected salt, or exposing the salt on platinum wire to the flame of the blow-pipe ; when, if soda be present, a rich and pure

yellow colour will be given to the flame. Of late it has been found that a solution of antimoniate of potash, which cannot of course affect the salts of potash, causes a white precipitate in solutions of those of soda, even when very diluted. Unfortunately the test does not keep well, and must be prepared as it is required.

The chief uses of soda are in the manufacture of glass and of hard soap. The carbonate is used in washing, and is a powerful detergent, although milder than carbonate of potash.

## SODIUM AND CHLORINE.

Chloride of Sodium.  $\text{Na Cl} = 58.5$ .

SYN. *Muriate of Soda*.—*Sea-Salt*.—*Rock-Salt*.—*Kitchen Salt*.—This very important salt is formed when chlorine and sodium, or hydrochloric acid and soda, come together. But it is found in immense quantity, dissolved in sea-water, and in the water of salt springs, and in smaller quantity in all natural waters, by which, indeed, it is carried to the sea, where it accumulates. Inland seas, without any outlet, and where consequently, the superfluous water escapes only by evaporation, become more saline than sea-water, although the streams which feed them are not richer in salt than ordinary rivers. Hence the Dead Sea, in Palestine, fed by the Jordan, is a very strong brine, containing the same ingredients as sea-water, but far more of them, these ingredients being also the same which are found in the Jordan and all rivers, in much smaller quantity. Salt is also found abundantly, as rock-salt, in various countries. It is obtained from the sea-water by simple evaporation, either spontaneous, or with the aid of heat, till crystals separate, which are nearly pure chloride of sodium.

The most celebrated salt mines are those of Cheshire and Gloucestershire, in England; of Salzburg, in the Tyrol; of Cardova, in Spain; and of Wielitzka, in Poland. The last-named is of enormous extent, and capable of supplying the world for ages. Rock-salt also occurs in other parts of the world, as in Nova Scotia. It is usually a member of the new red sandstone formation, and is accompanied there by beds of gypsum; but the immense deposit of Wielitzka is said to occur in the chalk formation. The salt, when tolerably pure, is brought out in blocks, which, if necessary, are dissolved and crystallised. When mixed, as it often is, with much clay, it must be dissolved, either in the mine, where the solution is pumped out for evaporation, or outside. In some places, as at Prestonpans, rock-salt,

which need not be very pure, from a distance, is dissolved in sea-water so as to form a solution strong enough to be economically evaporated artificially. In other places, especially in volcanic formations, salt is extracted from saline springs, which, if strong, are at once evaporated by fires ; but, if weaker, are first concentrated by graduation, that is, by allowing the water to trickle over large surfaces covered with twigs, and exposed to the wind. It is pumped up to the reservoir above, and the operation is repeated till the concentration is sufficient. This is done at Kreuznach, at Roehme, at Nauheim, and in other places. Lastly, salt is extracted from sea-water, in warm climates, by spontaneous evaporation, as on the south-west and south coasts of France. When rapidly evaporated, the solution yields small granular crystals, or table salt ; when more slowly formed, there is obtained the coarse kitchen salt, or that used in curing meat and fish ; while bay-salt consists of larger crystals, formed by spontaneous evaporation. In all cases, the mother liquid left after crystals cease to form, which is called *bittern*, contains chloride of magnesium and bromide of sodium or magnesium.

The properties of salt are well known. It is singular that it is not materially more soluble in hot than in cold water, for which reason it separates in crystals from the hot liquid during evaporation, and ought to be taken out from time to time with a perforated ladle, to allow the mother liquid to drain off.

One chief use of salt is as an antiseptic in curing meat. It seems to act chiefly by removing so much water from the flesh that too little is left to allow of putrefaction. Hence, highly salted meat is always dry, and requires long steeping in water to render it eatable. Salt is also employed to yield hydrochloric (muriatic) acid, and chlorine, for the making of bleaching-powder, as well as the best carbonate of soda. In preparing hydrochloric acid from salt, which is done by the aid of oil of vitriol, sulphate of soda is formed, from which, by heating it with charcoal, carbonate of soda is obtained. Thus in the very important manufacture of soda from salt, both the chlorine and the sodium are made use of ; the hydrochloric acid being but a secondary product, formed in the first stage of the manufacture of carbonate of soda, a product nearly equal in importance to the oil of vitriol, by means of which it is made.

But the most important use of salt, which renders it an absolute necessary of life to animals in some shape or other, is as a condiment to food, or rather, as a substance indispensable to digestion. This subject will be fully treated of in the Second



Part of this work : in the meanwhile, it may be mentioned that the free muriatic acid, always present in the chyme before it leaves the stomach, and the soda which is found in the chyle and in the blood, and which is the essential basic element of the bile, are both derived from salt, either originally present in the food, or, as is most commonly the case, added to it by man. Herbivorous animals, who produce an enormous quantity of bile, find salt in their food, and above all in the river or spring-water they drink. But they are so sensible of the good effects of salt, that they show the greatest preference for salt springs, and indeed for solid salt, if placed within their reach. When supplied with salt in moderate quantity they thrive uncommonly well, as in salt marshes, which are well known to give rise to very rich and well-feeding pastures. An excess of salt is, however, injurious.

#### SODIUM WITH BROMINE, IODINE, AND FLUORINE.

The compounds of sodium with these elements are quite analogous to those of potassium above described. The iodide and bromide of sodium are found in sea-water and in salt springs in minute quantity. The formulæ of these three compounds are  $\text{NaBr}$ ,  $\text{NaI}$ , and  $\text{NaF}$ .

#### SODIUM WITH SULPHUR.

Sodium, like potassium, unites with sulphur in several proportions. The protosulphuret,  $\text{NaS}$ , is very similar to the corresponding sulphuret of potassium ; the others are little known.

It is very remarkable that the beautiful mineral, lapis lazuli, or ultra-marine, the nature of the colouring matter in which was long a complete puzzle to chemists, should, according to recent discoveries, owe its magnificent blue colour to the presence of sulphuret of sodium, a compound destitute of any such colour. But this seems to be really the case : for by heating a mixture of hydrated alumina and silicic acid to whiteness, along with sulphuret of sodium, C. G. Gmelin has succeeded in obtaining artificial ultra-marine, which is now prepared in France and Germany, quite equal to the native pigment, and very much cheaper. We are still quite in the dark as to the true nature of the blue compound formed in this operation.

The compounds of sodium with phosphorus, carbon, boron, and silicon are unknown. With silicic acid, soda, like potash, forms glass.

16. LITHIUM.  $\text{Li} = 6.95$ .

This metal is very rare, occurring only as oxide of lithia in a few rare minerals, such as spodumene, petalite, lepidolite, and lithion-mica. The metal has been obtained in small quantity by means of galvanism from the oxide, and is white, burning when heated, with a blood-red flame, and forming protoxide of lithium, or lithia.

Bunsen has lately prepared lithium by passing a powerful electric current through the fused chloride of lithium. It is white, melts at  $356^{\circ}$ , and is not volatilised by a red-heat. But its most striking property is its low Sp. G., which is no more than 0.5936, thus it is the lightest solid body known. We have now, therefore, at one extreme of the scale, lithium, Sp. G. 0.5936; at the other, platinum, Sp. G. 22, and iridium, said to have a density of nearly 25; and thus the lightest and the heaviest solids are both metals.

Protoxide of Lithium.  $\text{LiO} = 14.5$ .

SYN. *Lithia*.—This alkali can only be obtained from either of the above minerals, which are silicates. One part of the mineral in fine powder is mixed with two of fluor-spar, and the mixture heated with sulphuric acid, until the whole of the silica is dissipated. There then remains a mixture of sulphates of alumina, lime, and lithia, and in the case of lepidolite or spodumene, potash. By boiling with carbonate of ammonia in excess, the alumina and lime are precipitated, and the filtered liquid is evaporated to dryness, and ignited to expel the sulphate of ammonia. The residue is sulphate of lithia, or sulphates of lithia and potash. In the latter case, by the cautious addition of chloride of barium, the sulphuric acid is separated as sulphate of baryta, and the lithia and potash converted into chlorides. These being dried, are digested in absolute alcohol, which dissolves the chloride of lithium. The lithia is now free from other bases: to obtain it in the separate state, the chloride is converted into sulphate, by being boiled with oil of vitriol, and the solution of the sulphate decomposed by the exact equivalent of baryta-water, by which the sulphuric acid is precipitated, while the free lithia is dissolved, and the solution, if evaporated, leaves hydrate of lithia,  $\text{LiO}, \text{HO}$ .

Lithia is not quite so soluble in water as soda or potash, nor is it so caustic; but it very much resembles these alkalies. Its solution attracts carbonic acid as readily as theirs from the atmosphere. When lithia is fused on platinum, it corrodes and stains the metal. Lithia and all its salts give a blood-red colour

to flame. The carbonate of lithia is sparingly soluble, and its phosphate is nearly insoluble. Lithia occurs too rarely to admit of any useful application; but it is important to know that lithion-mica, which is recognised by its easy fusibility before the blow-pipe, and by its tinging the outer flame red, has hitherto been only found associated with albite and topaz, or pycnite, in tin districts, and its occurrence, thus associated, may be looked on as a sure indication of the existence of tin in the locality.

Chloride of lithium,  $\text{LiCl}$ , crystallises in cubes. It is very deliquescent and soluble in alcohol, the flame of which it colours of a fine red.

The three first metals form a group of three elements, corresponding to that of chlorine, bromine, and iodine, and according to the most recent determinations, the atomic weight of sodium is the exact mean between those of potassium and lithium. The analogy and graduated difference in properties are very strongly marked.

#### APPENDIX TO THE FIRST, OR ALKALINE GROUP OF METALS.

Ammonium.  $\text{NH}_4 = \text{Am} = 18$ .

This hypothetical compound metal has already been described under the head of Ammonia, but we must here consider it as a metal, analogous to the three just described.

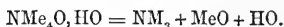
In all the salts of ammonia with oxygen acids  $\text{AmO}$  is found. This compound, oxide of ammonium  $= \text{NH}_3\text{HO}$ , is itself a very powerful and caustic alkali, and neutralises all the acids. It is important to observe that it is isomorphous with potash,  $\text{KO}$ ; so that the salt  $\text{KO}, \text{SO}_3$  has the very same form as  $\text{AmO}, \text{SO}_3$ .

Oxide of ammonium, although capable of neutralising the strongest acids, cannot exist in the separate form. If we attempt to separate it, it instantly splits up into water and ammonia;  $\text{NH}_4\text{O} = \text{NH}_3 + \text{HO}$ . The cause of this instability is obviously the very strong attraction of the oxygen for the fourth eq. of hydrogen, which, according to the law of affinity, is held by a feebler attraction than the remaining three. But in a remarkable class of compounds, discovered by Hofmann, we have evidence that oxides analogous to, and homologous with, oxide of ammonium, not only exist in the separate (hydrated) form, but have the most remarkable resemblance to caustic potash. For example, the hydrated oxide of tetramethylum,  $\text{NMe}_4, \text{HO}$ , is a caustic alkali, very like caustic potash,  $\text{KO}, \text{HO}$ . It is caustic, attracts water and carbonic acid from the air, and forms soaps

with oils. It is not decomposed on being isolated, because the attraction of the oxygen for the fourth eq. of methyle is not nearly so strong as in the case of hydrogen. But if we expose this oxide to heat, then we find that it undergoes precisely the same change as oxide of ammonium; for hydrated oxide of ammonium yields ammonia and water.



and hydrated oxide of tetramethylum yields trimethylamine, oxide of methyle and water; thus



In both cases the hydratic water remains unchanged, and the reaction is precisely analogous in the two cases, so that if the oxide of tetramethylum were separated at a high temperature, it would be found as unstable as oxide of ammonium is at the ordinary temperature. Possibly oxide, or hydrated oxide of ammonium, may be capable of existing in the separate form at very low temperatures, combined with great pressure. If so, we may be pretty sure that it will prove to be crystallisable and very caustic.

Chloride of Ammonium.  $\text{AmCl} = \text{NH}_4\text{Cl} = \text{NH}_3, \text{HCl} = 53.5.$

This is the well-known salt, sal-ammoniac, which is analogous to  $\text{KCl}$ ,  $\text{NaCl}$ , and  $\text{LiCl}$ , crystallising, like them, in cubes. It is the salt from which ammonia and all its compounds are formed, and it is prepared from the impure carbonate of ammonia obtained by distilling animal matters. It is entirely volatile, soluble in water, has a pungent saline taste, and no smell. Its chemical relations are those of a chloride, although it is called muriate of ammonia, because it is formed when muriatic (hydrochloric) acid and ammonia act on each other. But there is little doubt that these bodies mutually decompose each other, according to the equation,  $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$ . Chloride of ammonium, like chloride of potassium, forms double chlorides with the perchlorides of the metals of the platinum group. The platinum salt,  $\text{AmCl}$ ,  $\text{PtCl}_2$ , is not to be distinguished from  $\text{KCl}$ ,  $\text{PtCl}_2$  by its appearance. When heated, it leaves pure spongy platinum.

The bromide, iodide, and fluoride of ammonium are very similar to the chloride. The sulphides of ammonium, which are very like those of potassium, have been already described as most useful reagents.

## ORDER 2.—METALS OF THE ALKALINE EARTHS.

17. BARIUM.  $Ba = 68.5$ .

This metal may be obtained, according to Bunsen, by the action of a powerful electric current on the fused chloride of the metal. It is of a pale yellow colour, malleable, and fusible at a red heat. Its Sp. G. is not ascertained, but is probably about 5, as that of its protoxide is 4. Indeed it is named from the high Sp. G. of its native compounds, compared to other minerals of similar aspect. Barium soon tarnishes in air, being oxidised, and it decomposes water rapidly at ordinary temperatures.

Barium is not a very scarce element; for its sulphate, or heavy spar, is a mineral which is frequent in metallic veins, such as those of lead and copper; and also occurs in beds of considerable extent, as well as in veins, usually in trap rocks, in which it is the only mineral. In Ayrshire there is a small hill, said to consist chiefly of heavy spar. Carbonate of baryta, or witherite, is also not unfrequent, as, for example, in the Cumberland lead district.

Protoxide of Barium.  $BaO = 76.5$ .

SYN. *Baryta*.—This alkaline earth occurs in nature combined with carbonic and sulphuric acids, forming sulphate of baryta, or heavy spar, and carbonate of baryta, or witherite, as above-mentioned. It is best obtained pure by decomposing pure nitrate of baryta, by a continued red-heat, when the nitric acid is destroyed, being expelled as nitrous acid and oxygen, and the baryta left behind.  $BaO, NO_3 = BaO + NO_2 + O$ .

Baryta is a gray porous solid, the Sp. G. of which is about 4.000. It has an acrid alkaline taste, but is much less soluble in water than potash or soda. When sprinkled with water, it slakes, like quicklime, combining with the water to form a dry, white powder, hydrate of baryta,  $BaO, HO$ . Great heat attends this combination. Baryta, if exposed to the air, speedily attracts moisture and falls to powder, and the hydrate absorbs carbonic acid from the air, and is converted into carbonate by degrees.

Hydrate of Baryta.  $BaO, HO = 85.5$ .

This compound is formed when dry baryta is slaked with water as above mentioned. It is a bulky white powder, which dissolves in 3 parts of boiling water, and in about 20 of cold water. The saturated hot solution deposits, on cooling, crystals,

which are composed of  $\text{BaO}, \text{HO} + 9 \text{ aq.}$  The saturated cold solution, which is called barytic water, is a most useful test of the presence of carbonic acid in the air, or in any gas; for with that acid it instantly produces the insoluble carbonate of baryta, which forms a film, or crust, on the liquid.

A solution of baryta may be formed, extemporaneously, by boiling sulphuret of barium in solution with oxide of copper or oxide of lead in excess, and filtering as soon as the liquid gives a white, and not a black precipitate with acetate of lead. The change is as follows: with copper,  $6\text{BaS} + 8\text{CuO} = 5\text{BaO} + (\text{BaO}, \text{S}_2\text{O}_2) + 4\text{Cu}_2\text{S}$ ; the hyposulphite of baryta and the disulphide of copper being both insoluble; with lead,  $\text{BaS} + \text{PbO} = \text{BaO} + \text{PbS}$ . The sulphuret of lead, being insoluble, is easily separated by the filter, as well as that of copper and the hyposulphite.

Baryta may be recognised, either in the free state, or in its salts, by its giving, with alkaline carbonates, a white precipitate of carbonate, and with sulphuric acid or any soluble sulphate, a white precipitate of sulphate of baryta. The latter is quite insoluble in water and acids: and hence baryta and its salts are much used as tests for sulphuric acid, while both baryta and sulphuric acid are quantitatively estimated by converting them into the sulphate. Baryta and all its soluble salts are very poisonous. The carbonate, though almost perfectly insoluble in water, is also very poisonous, being probably dissolved by acids present in the stomach.

Peroxide of Barium.  $\text{BaO}_2 = 84.5$ .

This oxide is formed either by passing oxygen over baryta at a red-heat, or by sprinkling chlorate of potash on baryta heated to a very low redness, and washing away the soluble part with water. In the latter case it is obtained as a hydrate. It is insoluble in water, and weak acids dissolve it, forming a salt of protoxide; while the oxygen combines with water, forming a peroxide of hydrogen. In fact, the peroxide of barium is only used for the purpose of making that compound.

Boussingault has suggested the use of peroxide of barium to obtain oxygen from the atmosphere. Baryta is heated to low redness in a current of air till it becomes peroxide; it is then strongly ignited, when the newly absorbed oxygen is expelled and collected, baryta being reproduced. These operations may be alternated with the same portion of baryta any number of times; and in an apparatus devised by Boussingault for the purpose, atmospheric oxygen can thus be obtained in considerable quantity. It is probable, however, that the cost

of the fuel required will render oxygen so prepared more expensive than that obtained from the peroxide of manganese, or even from the chlorate of potash, which latter salt is now manufactured at a wonderfully low price, and very pure.

## BARIUM AND CHLORINE.

Chloride of Barium.  $\text{BaCl} = 104$ .

This salt is best obtained by dissolving carbonate of baryta in hydrochloric acid,  $\text{BaO}, \text{CO}_2 + \text{HCl} = \text{BaCl} + \text{HO} + \text{CO}_2$ . It is also obtained by acting on solution of the sulphuret of barium with the same acid,  $\text{BaS} + \text{HCl} = \text{BaCl} + \text{HS}$ . In the former case carbonic acid gas, in the latter sulphuretted hydrogen gas, is disengaged; and in both the chloride of barium remains dissolved, and, on evaporation, crystallises in white brilliant tabular crystals, which are composed of  $\text{BaCl} + 2 \text{aq}$ . A red heat expels the water of crystallisation, and chloride of barium is left.

It is a white solid, soluble in water, and is used in medicine, and very extensively in chemistry, as a test for sulphuric acid, and a means of removing that acid from any solution, and also of determining its quantity.

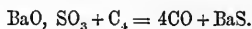
Bromide, iodide, and fluoride of barium are very analogous to the chloride. Silicofluoride of barium,  $\text{BaF}, \text{SiF}_3$ , is deposited in minute crystals nearly insoluble, when fluosilicic acid is added to a salt of baryta.

The soluble salts of barium colour flame a dingy yellow.

## BARIUM AND SULPHUR.

Sulphuret of Barium.  $\text{BaS} = 84.5$ .

This useful compound, from which all the other compounds of barium may be obtained, is prepared from the native sulphate of baryta, or heavy spar, by reducing it to fine powder, mixing it with  $\frac{1}{6}$ th of its weight of lamp black (charcoal), and exposing the mixture to a white-heat for two hours in a covered crucible. The following change takes place:—



The sulphuret of barium dissolves in hot water, forming a colourless solution, which, on cooling deposits crystals of the sulphuret, as a hydrate,  $\text{BaS} + 6\text{HO}$ . The solution, if exposed to the air, gradually absorbs oxygen, becoming yellow, and is finally converted into hyposulphite of baryta, the latter salt being deposited in hard brilliant crystals. When, in

preparing the sulphuret, the heat has been insufficient, the sulphuric acid of the sulphate of baryta is entirely deoxidised, the baryta only partially, and we obtain a mixture of baryta and persulphuret of barium,  $\text{BaS}_2$ . Thus  $2 (\text{BaO}, \text{SO}_3) + \text{C}_8 = \text{C} + 7 \text{CO} + \text{BaO} + \text{BaS}_2$ . This mass, dissolved in hot water, deposits, on cooling, crystals of hydrate of baryta: while the solution, owing to the presence of persulphuret, is orange-coloured.

Sulphuret of barium from its solubility, and from its being easily decomposed, serves to prepare all the compounds of barium. Thus, as already stated, if boiled with oxide of copper or of lead, it yields hydrate of baryta; and oxide of manganese may be used for the same purpose. With hydrochloric acid it yields chloride of barium, and with nitric or acetic acid it gives rise to nitrate or acetate of baryta,  $\text{BaS} + \text{HO}, \text{NO}_5 = \text{HS} + \text{BaO}, \text{NO}_5$ . Mixed with carbonate of potash, soda, or ammonia, in solution, it produces insoluble carbonate of baryta, and a soluble sulphuret of potassium, sodium, or ammonium,  $\text{BaS} + \text{KO}, \text{CO}_2 = \text{KS} + \text{BaO}, \text{CO}_2$ . From the nitrate pure baryta, and from the carbonate, any salt of baryta may be obtained.

Of late years, carbonate of baryta is often added to the usual ingredients of plate and flint-glass, as a substitute for part of the alkalis usually employed. It is of course converted into silicate. Chlorate of baryta has been employed in Pyrotechny; showing in perfection the characteristic green flame of barium compounds.

#### 18. STRONTIUM. $\text{Sr} = 43.8$ .

Strontium is a much less abundant metal than barium, but is yet found in considerable quantity. It is very analogous to barium in its relations, and occurs, like it in the form of sulphate of strontia or celestine, which is abundant in Derbyshire and in Sicily; and in the form of carbonate of strontia, or strontianite, which is so named because it was first found in a lead mine at Strontian, in Argyllshire. The metal is procured in the same way as barium, by the action of a Bunsen's battery on the fused chloride. It has, like barium, a pale yellow colour, and is much lighter, its Sp. G. being 2.54. When heated in air it burns with a reddish-yellow flame, and with scintillations, and it decomposes water at ordinary temperatures. It is not acted on by concentrated nitric acid, but the diluted acid dissolves it. Its compounds resemble those of barium, as the metal resembles barium, in the same degree as sodium and its compounds resemble potassium and its compounds.



Protoxide of Strontium.  $\text{SrO} = 51.8$ .

*Syn. Strontia.*—This oxide, like baryta is obtained by treating the nitrate. It forms a gray porous mass, exactly like baryta. It also slakes, with evolution of much heat, when sprinkled with water, falling to a bulky dry snow-white hydrate of strontia,  $\text{SrO},\text{HO}$ . This hydrate dissolves in boiling water, and the saturated solution, on cooling, deposits large transparent crystals, which are  $\text{SrO},\text{HO} + 9 \text{ aq.}$  The 9 eqs. of water of crystallisation are expelled by heat, but not the eq. of combined water. These crystals require 50 parts of cold and only 2 of boiling water to dissolve them. The solution is strongly alkaline, and absorbs carbonic acid from the air, forming the insoluble carbonate.

Chloride of Strontium.  $\text{SrCl} = 79.3$ .

This salt is obtained exactly in the same way as the chloride of barium; either from the carbonate or from the sulphide by the action of hydrochloric acid. It is very soluble, and forms acicular crystals,  $\text{S}_2\text{Cl} + 6 \text{ aq.}$ , which are deliquescent. It dissolves in alcohol, to the flame of which it gives a fine crimson tint.

The iodide, bromide, and fluoride of strontium possess no special interest. The silicofluoride of strontium,  $\text{SrF},\text{SiF}_3$ , is soluble, and this renders fluosilicic acid a good test for distinguishing strontium from barium in solution. In the case of barium, insoluble crystals are deposited after a short time.

Sulphide of Strontium.  $\text{SrS} = 59.84$ .

This sulphide is easily obtained, like that of barium, by igniting strongly, in a covered crucible, a mixture of finely powdered sulphate of strontia with about  $\frac{1}{3}$ th of its weight of charcoal. The ignited mass dissolves, with the exception of any excess of charcoal, in boiling water, and from this solution, the chloride of strontium, the nitrate and acetate of strontia, hydrate of strontia, and carbonate of strontia, may be easily prepared, as explained under barium.

The compounds of strontium were long confounded with those of barium, till Hope, and about the same time, Klaproth, demonstrated that they contained an analogous, but peculiar base. Two characters serve to distinguish them, in spite of their remarkable similarity; namely, the much greater density of barium, and the fine red colour given to flame by the salts of strontium. The absence of poisonous properties in the latter, the form of the crystallised chloride, its deliquescence,

and the solubility of silicofluoride of strontium, as well as of hyposulphite of strontia, are also marks of difference. The sulphate of strontia is also not absolutely insoluble as that of baryta is.

The only use to which strontium is applied is that in the form of nitrate; it is used in preparing red fire, such as is seen in the theatres, and mixtures for red fire signals and rockets, &c.

#### 19. CALCIUM. $\text{Ca} = 20$ .

This metal is far more abundant than the two preceding, and is indeed one of the most abundant elements in nature. It occurs chiefly in the form of carbonate of lime (lime is the protoxide of the metal), which appears as marble, limestone, and chalk, in very extensive beds in almost every geological formation. Carbonate of lime also occurs dissolved in water, as in sea-water, and in most springs; sometimes in large proportion, being dissolved by excess of carbonic acid. Water strongly charged in this way, on exposure to air, soon loses carbonic acid, and the carbonate is deposited, encrusting all objects over which it flows. Such objects are often said to be petrified, but properly speaking, they are only encrusted. In this way are formed the various deposits known as stalactites and stalagmites, when they are produced in caverns where the water enters from above; calcareous tufa, and travertine, which are abundantly deposited in many volcanic lakes. Carbonate of lime occurs also diffused through many soils, and constitutes the earthy part of the shells of mollusca, crustacea, and the microscopic foraminifera or polythalamia. It exists also, in small proportion, in the bones of animals, at all events in calcined bones, of which the chief ingredient is phosphate of lime. In magnesian limestone or dolomite, carbonate of lime is combined with carbonate of magnesia. Calcium also occurs abundantly in the form of sulphate of lime, as gypsum alabaster, or, when in large foliated crystals, selenite. Lastly lime is an ingredient, in the form of silicate, of many siliceous rocks and minerals, and in fluor-spar calcium is found combined with fluorine.

Calcium is obtained by the action of a Bunsen's battery on a fused mixture of 2 eqs. chloride of calcium with 1 eq. chloride of strontium. As it is separated, it is protected from the air by so regulating the heat that a layer of the chloride on the surface solidifies. It has the pale yellow colour of an alloy of gold with silver, is very malleable, softer than gold, has the Sp. G. 1.578, and is fusible at a red heat. When exposed to

dry air, it slowly tarnishes by oxidation, and more rapidly in moist air. When heated to redness in the air, it burns with a brilliant white light, and with scintillations. It also burns with vivid light, if heated in chlorine, or in the vapours of bromine, iodine, or sulphur. It decomposes water rapidly, and is dissolved by diluted nitric acid, but not acted on by the concentrated acid. It readily amalgamates with mercury.

Protoxide of Calcium.  $\text{CaO} = 28$ .

*SYN. Lime.*—This base, as already mentioned, is very abundant in nature, in the forms of carbonate, sulphate, and phosphate. The latter salt not only forms the earthy part of bones, but is found in the ashes of all plants; and is, in fact, universally diffused through rocks and arable soils.

Pure lime is easily obtained by igniting pure marble, limestone, or chalk, till all the carbonic acid is expelled. This process requires the aid of a current of air, and in limekilns this is obtained by stratifying the limestone with the fuel. The residue is pure or quicklime. This residue is seldom quite white, but combines with water to form a snow-white hydrate (slaked lime). A high temperature is produced in the slaking of lime. Lime is far less soluble in water than baryta, or strontia, and cold water dissolves a good deal more lime than hot, about  $\frac{1}{600}$ . The solution is called lime-water; it tastes acrid, and if exposed to the air, is soon covered with a film of carbonate, which forms a crust that at length breaks. Quicklime, exposed to air, gradually absorbs both water and carbonic acid; but a good red-heat always restores it to the state of quicklime again. When an excess of hydrate is mixed up with water, it forms a milky-looking fluid, called milk or cream of lime, which is much used for absorbing carbonic acid.

The uses of lime are well known: slaked lime is the chief ingredient in mortar, which is an intimate mixture of slaked lime with 3 or 4 parts of sharp sand, made into a paste with water. It has the important property of gradually hardening when exposed to air, though in building the hardening is chiefly external, where a little silicate of lime is formed, which coats the sand, and acts as a cement. The lime near the surface absorbs carbonic acid slowly, but within it remains, even for centuries, in the form of hydrate. The good quality of mortar depends chiefly on the selection of the materials, and on their being very intimately mixed. If the sand be too finely divided, the mortar is bad. The Romans, and those who built the fortresses of the dark and middle ages, took very great pains to secure good mortar, so that it is quite common

to find, in ruins of the period referred to, masses of building so firmly knit together, that they will break more readily through the middle of a stone than at the junction of two stones. In modern buildings, from motives of economy, the quality of mortar is often inferior to what it ought to be.

Hydraulic mortar, which hardens under water, is made by adding to ordinary lime certain kinds of clay, such as *puzzuolana*, a volcanic clay found near Naples. Portland cement is made by burning a mixture of chalk and a clay from the valley of the Medway. Carbonate of magnesia, added to lime, also gives it hydraulic properties. There are various natural limestones, containing variable proportions of clay or silicate of alumina, which, when calcined, yield hydraulic lime.

Lime is also extensively used in agriculture, where it exerts as hydrate, into which the quicklime is soon converted by the air and by rain, a most important action on the soil. It causes the partial decomposition of felspar, which contains silica as well as potash in an insoluble form, and thus renders these elements soluble and available for plants. This is easily shown by mixing finely-powdered felspar with slaked lime and water. In a short time free potash may be detected in the water. The idea that lime was useful by hastening the oxidation of the organic matter in the soil, is no longer entertained. It does hasten the oxidation of such matter, but it is desirable that the soil should always contain organic matter in a state of slow decay, yielding carbonic acid to act as a solvent, whereas that which is oxidised by the lime is dissipated before the plant can employ the carbonic acid thus formed.

Lime is employed also in preparing caustic potash and soda, as in soap making. It is an ingredient of the flux used in smelting iron and some other metals; it is also one of the ingredients of glass, and lime-water is used in medicine as an antacid. With acids lime forms salts, of which the carbonate, like that of baryta or strontia, is insoluble, the chloride very deliquescent, and the sulphate sparingly soluble, but far from insoluble. Lime and its salts are recognised by forming, with oxalate of ammonia, the very insoluble oxalate of lime. In testing for lime, the solution must be neutral, as an excess of acid dissolves the oxalate.

Chloride of Calcium.  $\text{CaCl} = 55.5$ .

This salt is formed when carbonate of lime is dissolved in hydrochloric acid, as in preparing carbonic acid gas,  $\text{CaO}, \text{CO}_2 + \text{HCl} = \text{CaCl} + \text{HO} + \text{CO}_2$ . When the neutral solution is evaporated to the consistence of syrup, it forms on standing in a

cold place, long prisms of crystallised chloride of calcium,  $\text{CaCl} + 2\text{HO} + 4 \text{ aq.}$  At  $480^\circ$  these lose the 4 equivalents of water of crystallisation, and at a red-heat the other two equivalents of water. The crystals, when powdered and mixed with snow, liquefy rapidly, and produce intense cold. In every form, chloride of calcium has a great attraction for water, and it is much used for drying gases, and in organic analysis for collecting the water, by weighing which the proportion of hydrogen is determined. But it cannot be used to dry ammonia, because it absorbs that gas, forming a compound  $\text{CaCl} + 4\text{NH}_3$ . It also serves to deprive alcohol, ether, and many similar fluids, of water.

The bromide and iodide of calcium are deliquescent salts,  $\text{CaBr}$  and  $\text{CaI}$ .

Fluoride of Calcium.  $\text{CaF} = 38.9$ .

This is a tolerably abundant mineral, occurring chiefly in veins along with lead ore, heavy spar, and quartz. It is well known as fluor, or Derbyshire spar, and crystallises beautifully in cubes, octahedrons, and tetrahedrons, which are transparent and colourless, or purple, green, brown, or yellow. It also occurs in a massive semi-crystalline form, capable of being cut and polished for ornaments. It is very remarkable that fluoride of calcium is an ingredient of bones in variable quantity. It is said to be found chiefly in the enamel of the teeth, and it is certainly found in variable quantity, but always present, in ancient human bones. It is now said that it is less easily detected in recent bones, owing to the presence of animal matter. It has been found in some bones to the amount of 10 per cent. It has now been detected, by Dr. G. Wilson, in small quantity in most rocks and waters, as well as in most animal and vegetable substances.

The presence of it is detected by treating the mineral or bone after ignition with oil of vitriol in a platinum crucible, covered with a waxed plate of glass, having the glass exposed by tracings made with a point through the wax. In a short time the tracings are so far etched as to be indelible, and very small traces of fluor-spar may be thus detected.

Sulphuret of Calcium.  $\text{CaS} = 36$ .

This compound is formed by a process similar to that given for sulphuret of barium. Sulphate of lime, mixed with  $\frac{1}{4}$  of its weight of charcoal powder, is strongly ignited for an hour or two in a covered crucible.  $\text{CaO}, \text{SO}_3 + \text{C}_4 = 4\text{CO} + \text{CaS}$ .

It is a nearly white powder, provided no excess of charcoal is present, and is very sparingly soluble in water. When it has

been exposed to the sun's rays, it shines in the dark, and is called Canton's phosphorus. When water, lime, and sulphur are boiled together, there is formed a yellow or orange solution containing hyposulphite of lime and pentasulphuret of calcium,  $3\text{CaO} + \text{S}_{12} = 2(\text{CaS}_5) + (\text{CaO}, \text{S}_2\text{O}_2)$ . This liquid, acted on by hydrochloric acid, yields persulphuretted hydrogen. When sulphur and lime are melted together, there is formed a mixture of sulphate of lime and sulphuret of calcium.

Phosphuret of calcium is obtained, in an impure state, by bringing the vapour of phosphorus in contact with red-hot lime. A brown powder is formed, which is a mixture of phosphate of lime and phosphuret of calcium,  $11\text{CaO} + \text{P}_7 = 2(\text{PO}_3, 2\text{CaO}) + 5(\text{Ca}_3\text{P})$ . When thrown into water it produces spontaneously inflammable phosphuretted hydrogen, along with hypophosphite and phosphate of lime. In moist air it falls to a brown powder, which is a hydrate. This, when it acts on water, yields the non-spontaneously inflammable form of phosphuretted hydrogen.

The three metals last considered, barium, strontium, and calcium, form a group of three elements, exhibiting the same analogies as we have observed in two other similar groups, namely, that of chlorine, bromine, and iodine, and that of potassium, sodium, and lithium. Indeed the analogy is quite as perfect between the three metals of the alkaline earths as between the three metalloids, for the atomic weight of strontium is the mean between those of barium and calcium, as that of bromine is the mean between those of chlorine and iodine; while the equivalent of sodium is the mean between those of potassium and lithium. In other points the three groups are equally remarkable, and it is quite conceivable that they may hereafter be shown to be portions of homologous series, and of course compound.

#### 20. MAGNESIUM. $\text{Mg} = 12\cdot2$ .

This metal is best obtained by decomposing, by the current from a battery of Bunsen's elements (zinc and charcoal), the fused chloride of magnesium at a red heat. The electrodes are of charcoal, and the negative one is hollowed out, that the reduced metal may collect in the cavity. It is apt, from its low density, to rise to the surface of the melted chloride, and there to be reoxidised.

It is a silver-white metal, Sp. G.  $1\cdot7$ , rather hard, malleable, and fusible at a red heat. It is hardly altered by dry air in the cold, but is oxidised slowly in moist air. When ignited in air or in oxygen, it burns with an intensely brilliant light;

the oxide thus formed is in no part fused. Cold water slowly acts on it; diluted acids dissolve it readily. It burns very brightly when heated in chlorine, or in the vapour of bromine, iodine, or sulphur.

Magnesium is a very abundant metal, though less so than calcium. It occurs in the form of pure carbonate of magnesia, in beds; also in magnesian limestone or dolomite,  $(\text{CaO}, \text{CO}_2) + (\text{MgO}, \text{CO}_2)$ , which is found in extensive strata, and it is an ingredient, chiefly in the form of silicate, of many rocks, such as trap-rocks and serpentine, and of a large number of minerals, such as talc, steatite, augite, and hornblende, the two latter of which are very abundant minerals, both pure and disseminated in rocks. Boracite is a borate of magnesia. Chloride of magnesium is the principal salt in the bittern, or mother liquor of sea-water and of salt springs; and sulphate of magnesia is abundant in certain mineral waters, as those of Epsom and Cheltenham.

#### MAGNESIUM AND OXYGEN.

Oxide of Magnesium.  $\text{MgO} = 20.2$ .

*SYN. Magnesia; Calcined Magnesia.*—This oxide occurs in nature as carbonate, forming considerable masses of rock in some parts of the world; also as a mixed carbonate of lime and magnesia, under the forms of dolomite and magnesian limestone; and as sulphate of magnesia, or Epsom salts, which occurs in many saline springs.

It is best obtained pure by heating the carbonate to redness. Pure or calcined magnesia is a bulky white powder, insoluble in water. It has an earthy taste, and readily unites with acids, neutralising them, on which account, and because it is in itself mild in its action, it is much used in medicine as an antacid. Magnesia, when precipitated from its salts by an alkali, combines with water, forming a hydrate,  $\text{MgO}, \text{HO}$ , which loses its water in a low red-heat. It is similar in appearance to the anhydrous base. This hydrate is found native crystallised.

Of the salts of magnesia, the carbonate, like that of the three preceding earths, is insoluble; but the sulphate is very soluble. The solution of this, or any other soluble salt of magnesia, is precipitated by potash, soda, and ammonia, which throw down pure magnesia; and by carbonates of potash and soda which form carbonate of magnesia. But carbonate of ammonia causes no precipitate, owing to the formation of a soluble double salt; and for the same reason, oxalate of ammonia does not precipitate the salts of magnesia. By this last character magnesia may be distinguished and separated from lime. The most delicate test

of magnesia in solutions is to add, first, carbonate of ammonia, and then phosphate of soda, which then forms an insoluble double phosphate of ammonia and magnesia, in the form of a heavy crystalline powder, slowly formed when the quantity of magnesia is very small, but quite insoluble in water containing a small quantity of free ammonia. The salts of magnesia, generally, have the same constitution as those of oxide of zinc, with which they are isomorphous.

Besides its uses in medicine, where it is employed as an antacid and laxative, magnesia is a useful ingredient of all fertile soils. The double phosphate of ammonia and magnesia is found in the husks of grain, and in the potato; and phosphate of magnesia is also found in bones. In a soil totally destitute of magnesia, grain does not produce perfect seed, however well the plants may thrive or grow in the stalk or leaf, to which parts magnesia seems not to be essential. Owing to the occurrence of the double phosphate in potatoes, bran, which contains that salt, is a very powerful manure for that crop.

#### MAGNESIUM WITH CHLORINE, BROMINE, IODINE, AND FLUORINE.

Chloride of Magnesium.  $\text{MgCl} = 47.7$ .

This salt is best formed as follows:—Take two equal portions of hydrochloric acid, and neutralise one with magnesia, the other with ammonia; then mix, evaporate to dryness, and ignite in a covered crucible till the sal-ammoniac is dissipated. Fused chloride of magnesium remains, which is poured out on a clean stone, and when solidified kept in a closely-stopped bottle. It is highly deliquescent, and is used for preparing magnesium.

When magnesia acts on hydrochloric acid, they combine, producing hydrochlorate of magnesia,  $\text{MgO}$ ,  $\text{HCl}$ , a rare case. On evaporating the solution to dryness and heating it, hydrochloric acid is expelled and magnesia is left. But when sal-ammoniac is added (chloride of ammonium,  $\text{NH}_4\text{Cl}$ ), and the mixture evaporated, chloride of magnesium is formed, and unites with the sal-ammoniac, forming a double chloride,  $\text{MgCl} + \text{NH}_4\text{Cl}$ . When this is ignited, the sal-ammoniac is expelled, and chloride of magnesium is left. Chloride of magnesium exists in sea-water, and is found in the mother liquor of the crystals of salt.

The iodide and bromide of magnesium are very soluble; the fluoride is insoluble.

Sulphuret of magnesium may be obtained by a method similar to that given for sulphuret of barium. When pure, it is a white



brittle mass, partly soluble in water. When sulphide of potassium is added to a boiling solution of sulphate of magnesia, the sulphide of magnesium falls as a thick gelatinous mass. Magnesium is usually associated with the three preceding metals, but is distinguished from that group by forming a soluble sulphate, and an insoluble oxide and hydrate. In these properties, as in many others, it agrees closely with zinc, and, indeed, zinc and several other metals are associated with magnesium to form what is called the magnesian group. The sulphates of these metals crystallise chiefly in two forms, one of which is that of the sulphates of magnesia and zinc. All these sulphates form double sulphates with the sulphates of potash, soda, and ammonia, and these double salts are all isomorphous, having the same form as sulphate of magnesia and potash,  $\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{aq.}$

### ORDER 3.—METALS OF THE EARTHS PROPER.

#### 21. ALUMINIUM. $\text{Al} = 13\cdot7$ .

This metal may be obtained, like the last, by the action of potassium on the chloride. Chloride of aluminium is mixed with small fragments of potassium in a platinum crucible, the lid of which is wired down. Heat is then applied by means of a spirit-lamp, when a violent action ensues, and a dark-gray mass is left, from which water dissolves chloride of potassium, leaving aluminium as a dark-gray powder, which has considerable lustre. It is not easily melted; and when heated in the air, or in oxygen gas, it burns with a vivid light, forming alumina, which is a sesquioxide of the metal.

The form of aluminium just described, which was long the only one known, is probably an allotropic modification of it; for it has lately been obtained in a perfectly metallic state.

Dry and pure sesquichloride of aluminium is placed in a long and wide tube of hard glass. In front of it are placed porcelain trays, containing sodium, carefully freed from naphtha by means of bibulous paper. The sodium is melted, and the chloride is then distilled over it, the tube having been previously deprived of air by a current of hydrogen. A violent action takes place, aluminium is reduced in the trays, and a double chloride of aluminium and sodium is formed, which covers the metal. The trays are then introduced into a porcelain tube, through which hydrogen is passed, and strongly ignited, when the metal melts into globules. These are once more melted under the double chloride in a porcelain crucible and a button of aluminium is thus obtained.

Aluminium, in this state, is a white metal, nearly of the aspect of silver, or between that of silver and platinum, which melts in a strong red-heat. Its Sp. G. is 2·5, and when rolled, 2·7. It is somewhat hard, and very sonorous, malleable and even ductile. The fused metal crystallises on cooling, and the crystals seem to be regular octohedrons. It is quite permanent in dry air, and even when heated to whiteness it is only superficially oxidised. I have seen specimens of it soon covered with a white coating of oxide in moist air; but I do not know whether this may not have been due to the presence of impurity, possibly of a little sodium. Nitric acid has no action on it in the cold, and but little when boiled; but hydrochloric acid rapidly dissolves it, forming chloride. Alkaline solutions also dissolve it, with the aid of heat.

Aluminium forms alloys with copper, silver, and iron, but not with lead or mercury. Those with copper are white and very hard, and take a high polish. With carbon and silicon it also combines, forming compounds somewhat like cast-iron.

From its lightness and from its not being altered by contact with air, aluminium has been used as a material for small weights, usually made of platinum. It has also been proposed for the beams of delicate balances, and has the advantage of not being acted on by the vapours of nitric acid as brass is apt to be.

Aluminium is of all metals the most abundant, as it is the chief ingredient of alumina, which forms a part of almost all rocks, generally as felspar, but also in other forms. Clays of all kinds, brickclay, fireclay, chinaclay and pipeclay, consist chiefly of alumina, with some silica, potash, and oxide of iron; they are, in fact, decayed or weathered felspar.

#### ALUMINIUM AND OXYGEN.

Sesquioxide of Aluminium.  $\text{Al}_2\text{O}_3 = 51\cdot4$ .

SYN. *Alumina*.—This earth is very abundant in nature. It occurs crystallised as the sapphire and ruby; in a crystalline, but more massive form, as corundum or emery; and as the chief ingredient of felspar, of many minerals, and of all clay, as well as of slaty rocks, from which, indeed, clays are derived. Pipe-clay is the purest clay, but is not pure alumina, although approaching to it.

Pure alumina is best prepared as follows:—A solution of alum is precipitated by an excess of chloride of barium, by which means the sulphuric acid is separated, and chloride of

aluminum is left in solution with the chloride of potassium and the excess of chloride of barium. Alum ( $\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3\text{SO}_3$ ) with  $4\text{BaCl}$  yields  $4(\text{BaO}, \text{SO}_3) + \text{KCl} + \text{Al}_2\text{Cl}_3$ . On evaporation, water is decomposed, and hydrochlorate of alumina is formed,  $\text{Al}_2\text{Cl}_3 + 3\text{HO} = \text{Al}_2\text{O}_3, 3\text{HCl}$ . When the dry mass is ignited, the hydrochloric acid is expelled, and the alumina is left with the chlorides of potassium and barium, which are removed by water. It may also be obtained by heating to redness pure ammonia-alum,  $(\text{NH}_4\text{O}, \text{SO}_3) + (\text{Al}_2\text{O}_3, 3\text{SO}_3) + 24 \text{ aq.}$ ; when pure alumina is left.

Alumina may also be prepared from pure alum,  $(\text{KO}, \text{SO}_3) + (\text{Al}_2\text{O}_3, 3\text{SO}_3) + 24 \text{ aq.}$ , by adding to its solution an excess of carbonate of potash; the bulky gelatinous hydrate is to be well washed with hot water; then, as some potash always adheres to it, redissolved in hydrochloric acid, and precipitated by ammonia. The precipitate, bulky and gelatinous as before, must be thoroughly washed, dried, and ignited, when pure alumina is left in hard translucent lumps.

Pure alumina, as prepared by the two first methods, is a fine white powder, quite unalterable in the furnace fire, but it has been melted in the oxyhydrogen blowpipe, and on cooling yielded a mass like corundum. When precipitated from its solution in acids by alkalis, it forms a very bulky gelatinous hydrate, which, when dried at  $60^\circ$ , is  $\text{Al}_2\text{O}_3, 6\text{HO}$ ; if dried at  $100^\circ$  it becomes  $\text{Al}_2\text{O}_3, 3\text{HO}$ . Dry or anhydrous alumina, mixed with water, forms a plastic mass, which admits of being moulded. This property is given to clay by the presence of alumina, and is the foundation of the art of making porcelain or earthenware.

Alumina, after ignition, is almost insoluble in acids; but the hydrate readily dissolves in all strong acids, forming salts which have a peculiar astringent taste.

Alumina is precipitated, as hydrate, from its solutions by potash, soda, ammonia, and their carbonates; but the precipitate readily dissolves in an excess of the two first. Hydrosulphuret of ammonia, which precipitates none of the previously-described metallic oxides, causes in solutions of alumina a precipitate, which, however, is not a sulphuret, but the hydrate of alumina precipitated by the ammonia of the test.

Besides the use of alumina, in the form of clay, in pottery, it is much used in dyeing and calico-printing, from its attraction for vegetable colouring matters, and for the fibre of cloth. It forms a bond of union between the cloth and the dye, and fixes the latter on the former. It is said, in this, to act as a mordant, and is most generally used in the shape of alum or acetate

of alumina. When solution of alum is mixed with a colouring matter, and the alumina then precipitated by an alkali, the hydrate carries with it all the colouring matter, or the greater part of it, and forms what is called a lake. The water-colour termed lake is merely a lake made with some pink dye stuff, such as madder or logwood. Carmine is a lake of Cochineal. Corundum and emery, on account of their hardness, which is next to that of the diamond, are much used for grinding and polishing hard substances.

Alumina, from its crystalline form, and especially from the composition of its salts, is believed to be isomorphous with sesquioxide of iron,  $\text{Fe}_2\text{O}_3$ , and hence is called sesquioxide of aluminium. The different forms of clay, mentioned under aluminium, are silicates of alumina with excess of base, with potash, oxide of iron, and sometimes lime. They form with water a plastic mass, which when strongly ignited, retains its form, but acquires a stony hardness. Hence the use of clay in making bricks, pottery, china, tobacco-pipes, &c. The clay of which finest porcelain is made, is called kaolin, and is the result of the action of the weather on a very pure felspar. The composition of clay is fundamentally that of a hydrated sesquisilicate of alumina,  $2\text{Al}_2\text{O}_3 + 3\text{SiO}_2 + 4\text{aq.}$  As sesquioxides require 3 eqs. of acid to 1 of base to form neutral salts, clay is a basic salt.

Though alumina does not enter into the composition of organic matter, it is yet of the most essential importance to vegetation; first, because the presence of a certain proportion of clay in the soil is necessary to give the requisite degree of cohesion, and to absorb and retain water, so that the roots of plants may have a firm attachment, and that the soil may not easily become too dry; and secondly, on account of the valuable property it possesses of absorbing ammonia and its salts from the atmosphere as well as from water; thus retaining within reach of the plants large quantities of ammonia which would otherwise be carried off. So great is the power of alumina in absorbing ammoniacal salts, that if water, containing a certain portion of them be filtered through a portion of ordinary clay soil, it passes through deprived of ammonia, and indeed purified from soluble organic impurities. The sesquioxide of iron in soils has a similar action, and assists in producing these results. Even a highly calcareous soil, if it contain, as is usually the case, only a small percentage of alumina and sesquioxide of iron, retains nearly all the ammonia that comes in contact with it. The ammonia is readily given up to plants, being apparently absorbed mechanically, in the same way as by charcoal.

## ALUMINIUM AND CHLORINE.

Sesquichloride of Aluminium.  $\text{Al}_2\text{Cl}_3 = 133.9$ .

This compound is prepared by passing chlorine gas over a mixture of alumina and charcoal, heated to redness in a tube. The chloride sublimes into the cold part of the apparatus. It forms a volatile crystalline mass, colourless or slightly yellow. It fumes in the air, and dissolves in water with much heat. It appears at first to combine with the water, forming a hydrated chloride,  $\text{Al}_2\text{Cl}_3, 3\text{HO}$ ; but on heating this, hydrochloric acid is expelled, and alumina is left,  $\text{Al}_2\text{Cl}_3, 3\text{HO} = \text{Al}_2\text{O}_3, 3\text{HCl}$ . The chloride is used for the preparation of aluminium.

The iodide, bromide, and fluoride of aluminium are little known. But a remarkable double fluoride, that of aluminium and sodium, is found in narrow beds on the coast of Greenland. It is a snow-white fibrous mass, a splinter of which readily melts in the flame of a candle. Hence it has been named cryolite, its formula is  $3\text{NaF} + \text{Al}_2\text{F}_3$ . When heated with sodium, the aluminium is reduced with ease, and it has been proposed to obtain aluminium in this manner.

The sulphuret of aluminium is formed when sulphur is dropped on red-hot aluminium. It is a dark-gray mass, which decomposes water, forming sulphuretted hydrogen and alumina, and hence its composition may be  $\text{Al}_2\text{S}_3$ . If so, we have  $\text{Al}_2\text{S}_3 + 3\text{HO} = \text{Al}_2\text{O}_3 + 3\text{HS}$ . Similar compounds are formed with phosphorus and selenium.

## 22. GLUCINUM. 23. YTTRIUM. 24. THORINUM. 25. ZIRCONIUM.

These metals, or rather their oxides, are all so rare as not to admit of any useful application. The oxides, which are glucina, yttria, thorina, and zirconia, only occur in a few rare minerals.

Glucina occurs in the emerald and in the beryl. Its composition is analogous to that of alumina; and its formula is  $\text{G}_2\text{O}_3$ . It is a white powder, insoluble in water, soluble in acids, forming salts, which have a sweetish taste. It resembles alumina very much, but differs from it in being soluble in solution of carbonate of ammonia. The metal, which may be obtained, like aluminium, from the chloride, has the Sp. G. 2.1, and is rather more fusible than silver. It is white and malleable, does not decompose water, even at a red-heat, but burns with amazing splendour when heated in oxygen.

Yttria, the oxide of yttrium, occurs in gadolinite, in yttrocerite, and in yttrotantalite. The pure earth is a white powder,

which dissolves in acids, forming sweetish salts, from which yttria is precipitated by alkalies ; but is not like alumina and glucina, redissolved by excess of potash or soda. It is, moreover, precipitated by ferrocyanide of potassium, while these earths are not. Yttria seems to be protoxide of yttrium,  $YO$ . The salts of yttria have often an amethyst colour ; but the recent researches of Mosander seem to show that this is owing to the presence of the oxide of one of the new metals detected by him, which accompany yttrium, namely, erbium, and terbium, both little known. It is probable that pure yttria is not yet known.

Thorina is still more rare, and has only been found in one mineral—thorite. It is a white powder, resembling yttria. The metal, thorinum, burns in air, or oxygen, when heated, with great splendour. It also burns with sulphur and phosphorus, as do the two preceding metals.

Zirconia is found in the zircon or hyacinth. It resembles alumina in appearance. It differs from all the preceding earths in being precipitated as an insoluble subsulphate, when solutions of its salts are boiled with sulphate of potash. The metal, zirconium, resembles the gray form of aluminium. The oxide is believed to be a sesquioxide  $Zr_2O_3$ . According to Svanberg, zirconia is not a pure oxide, but a mixture, probably of three oxides of unknown metals.

## METALS.—CLASS II.

ORDER 1.—METALS, THE PROTOXIDES OF WHICH ARE POWERFUL BASES, BUT WHICH DO NOT DECOMPOSE WATER, UNLESS WITH THE AID OF A RED-HEAT.

### 26. MANGANESE. $Mn = 27.6$ .

This metal occurs in considerable abundance, chiefly as deutoxide or peroxide  $MnO_2$ , which is much used in the arts and in chemical manufactures, as well as in the laboratory. It is besides universally diffused in small proportion in most rocks and soils. The metal is obtained by making oxide of manganese into a paste with oil, and exposing this paste to a strong white-heat in a covered crucible. If the heat be high enough, a button of the metal is obtained.

It is a hard, brittle, very difficultly fusible metal of a grayish white colour, Sp. G. 8.013. It tarnishes on exposure to the air, and is rapidly oxidised when heated. It decomposes water rapidly at a red-heat, hydrogen being disengaged. As a metal, it is not applied to any useful purpose.

## MANGANESE AND OXYGEN.

a. Protoxide of Manganese.  $\text{MnO} = 35.6$ .

This oxide is obtained when the peroxide is acted on by hydrogen gas at a red-heat. But the best method is to heat to redness a mixture of 1 part of dry chloride of manganese, 1 part of sal-ammoniac, and 2 parts of dry carbonate of soda. The chloride acts on the soda,  $\text{MnCl} + \text{NaO} = \text{MnO} + \text{NaCl}$ ; forming oxide of manganese and chloride of sodium: while the carbonic acid escapes as gas: the sal-ammoniac is also expelled, and its vapour serves merely to exclude the oxygen of the atmosphere. From the fused mass, water extracts the chloride of sodium; and leaves the protoxide of manganese undissolved.

It is a powder of a pale grass-green colour, which if prepared by hydrogen at a low red-heat, soon attracts oxygen from the air and becomes brown. If it has been made, however, at an elevated temperature, especially by the second process, it is more compact, and keeps tolerably well. When heated in the air, it takes fire and burns.

Protoxide of manganese is a powerful base, neutralising acids and forming salts, which are either colourless or have a tinge of flesh-colour. Its solutions give, with caustic alkalies, a precipitate of hydrate, which is at first white, but soon absorbs oxygen and becomes brown; with carbonated alkalies, a white precipitate of carbonate of manganese, which retains its whiteness till it is dried, when it becomes generally slightly fawn-coloured. Hydrosulphuret of ammonia causes a flesh-coloured precipitate of sulphuret of manganese, which, in the air, absorbs oxygen and becomes brown. Chloride of soda or bleaching liquor causes a bulky dark-brown precipitate of hydrated peroxide. The two last tests are characteristic. Ferrocyanide of potassium gives a white precipitate. All the salts of protoxide of manganese may easily be prepared from the carbonate, which again is most economically made from the chloride, the preparation of which will be described below. The sulphate is used in calico-printing.

b. Sesquioxide of Manganese.  $\text{Mn}_2\text{O}_3 = 79.2$ .

This oxide is a dark-brown powder, very similar to the peroxide, but rather lighter in colour, and yielding very little oxygen when ignited. It may be formed as a hydrate by passing a current of chlorine through carbonate of manganese suspended in water, and removing the unaltered carbonate by diluted nitric acid. It is a feeble base, and is only known to combine with

sulphuric acid, forming an amethyst-coloured solution of sesquisulphate. With sulphates of potash and ammonia, this salt forms manganese alums, which crystallise in dark purple octohedrons. When heated with sulphuric acid, it yields oxygen, and with hydrochloric acid, chlorine, but less of either than the peroxide (which see). As some specimens of peroxide are, naturally or accidentally, mixed with sesquioxide, the manufacturer finds it a source of inconvenience and loss. It occurs in nature in a pure state as braunite, and combined with baryta in psilomelane. Its hydrate is the mineral manganite. Its powder is dark brown.

c. Hyperoxide or Peroxide of Manganese.  $\text{MnO}_2 = 43.6$ .

SYN. *Deutoxide of Manganese*.—This oxide is found in considerable abundance, and is known in the mineral kingdom as pyrolusite. It generally assumes the form of a black shining mass composed of radiated groups of acicular crystals; also in distinct crystals, which are right rhombic prisms; and in the compact and even earthy state. Its powder is black. I have found nearly all the specimens I have examined to contain, besides iron, cobalt and nickel in small quantities. When heated to redness, it loses one-third of its oxygen, leaving red oxide;  $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$ . In a white-heat it is said to lose half its oxygen, leaving protoxide. Heated with oil of vitriol, it forms sulphate of protoxide, and half the oxygen is expelled.  $\text{MnO}_2 + \text{HO}, \text{SO}_3 = (\text{MnO}, \text{HO}, \text{SO}_3) + \text{O}$ . With hydrochloric acid it yields chlorine, chloride of manganese, and water.  $\text{MnO}_2 + 2\text{HCl} = \text{Cl} + \text{MnCl} + 2\text{HO}$ . It also yields chlorine when heated with common salt and sulphuric acid; and this is the process commonly used by the manufacturers of bleaching powder.  $\text{MnO}_2 + \text{NaCl} + 2(\text{HO}, \text{SO}_3) = (\text{MnO}, \text{HO}, \text{SO}_3) + (\text{NaO}, \text{HO}, \text{SO}_3) + \text{Cl}$ .

It is further used in glass-making to destroy the colour given to the glass by protoxide of iron, which it converts into peroxide; in larger proportion, to give glass an amethyst colour; and in numerous operations in the laboratory as a convenient oxidising agent.

With water, peroxide of manganese forms a hydrate,  $\text{MnO}_2, \text{HO}$ , which is obtained when salts of the protoxide are acted on by bleaching liquor, or when the acids of manganese are decomposed, whether spontaneously or by acids. It is a beautiful brown powder, which is decomposed by heat.

The commercial value of the peroxide depends on the quantity of chlorine it is capable of producing. This may be measured, either directly, by causing the chlorine to act on indigo, or by



causing it to convert protoxide of iron into sesquioxide ; or more indirectly by ascertaining the amount of carbonic acid produced when the peroxide is heated with sulphuric acid, oxalic acid and water. The reaction is  $\text{MnO}_2 + \text{SO}_3 + \text{C}_2\text{O}_3 = (\text{MnO}, \text{SO}_3) + 2\text{CO}_2$ , 1 eq. of peroxide thus gives 2 eqs. of carbonic acid, or just its own weight.

d. Manganic Acid.  $\text{MnO}_3 = 51.6$ .

This acid has not been isolated. It is only known in combination with bases, especially potash, in which state it forms the chief ingredient of the mass called chameleon mineral, formed by igniting peroxide of manganese strongly with nitre, or still better by heating a mixture of peroxide with its own weight of caustic potash. The ignited mass is dissolved in a little cold water, filtered through asbestos, and evaporated in vacuo over sulphuric acid, when it deposits green crystals, isomorphous with sulphate of potash. The green colour is a property of manganic acid and all its salts. The peroxide obtains oxygen from the nitre or chlorate of potash, and the acid when formed combines with the potash. Water dissolves the manganate of potash, forming a splendid emerald-green solution, which very soon begins to change colour, and passes through bottle-green, blue, and purple, to a fine crimson red, hydrated peroxide of manganese being at the same time deposited. The red colour belongs to a salt of the next acid, permanganic acid (see below). The salts of manganic acid are decomposed if kept in solution, depositing hydrated peroxide.

e. Permanganic Acid.  $\text{Mn}_2\text{O}_7 = 111.2$ .

The salt of this acid with potash, permanganate of potash, is formed, when the green mass obtained by heating the peroxide with nitre or with potash, which has been called mineral chameleon, from the changes of colour it undergoes, is dissolved in a large quantity of water. The best method is to mix together 4 parts of finely powdered peroxide with  $3\frac{1}{2}$  of chlorate of potash, to mix this with 5 parts of caustic potash, dissolved in as little water as possible, to dry the mixture, reduce it to powder, and expose it to a dull red-heat for an hour. The heated mass, which is deep green, nearly black, is dissolved in hot water. The green colour of the manganate changes to red, while hydrated peroxide separates. 3 eqs. of manganate of potash give rise to 1 eq. of permanganate, 1 of peroxide, and 2 of free potash :  $3(\text{KO}, \text{MnO}_3) = \text{MnO}_2 + (\text{KO}, \text{Mn}_2\text{O}_7) + 2\text{KO}$ . When the red solution is sufficiently evaporated, it deposits small dark bronze-coloured crystals of permanganate of potash.

This salt is more permanent than the manganate; but when we attempt to isolate the acid, it is rapidly decomposed, yielding hydrated peroxide and oxygen gas,  $\text{Mn}_2\text{O}_7 = 2\text{MnO}_2 + \text{O}_3$ .

The name of chameleon mineral was given to the compound above described from its singular changes of colour. Both the above acids possess and communicate to their salts very beautiful colours; but they cannot be used in dyeing, &c., because these acids are so easily decomposed, especially by the contact of organic matter. They ought to be filtered through asbestos when they require filtration.

f. Red Oxide of Manganese.  $\text{Mn}_3\text{O}_4 = 114.8$ .

This oxide occurs in nature as hausmannite, and may be obtained when any other oxide of manganese is strongly ignited in an open crucible. It is very permanent in composition: its colour is reddish-brown. It is not supposed to be an independent oxide of the metal, but rather a compound of two other oxides. It may be either  $\text{MnO} + \text{Mn}_2\text{O}_3$ , or  $\text{MnO}_2 + 2\text{MnO}$ , and it is not easy to say which.

g. Varvicite.  $\text{Mn}_4\text{O}_7 = 166.4$ .

This is another oxide, found native in Warwickshire, whence the name. It resembles the peroxide, but is really distinct. It is probably a compound of two others,  $\text{MnO}_3 + 2\text{MnO}_2$ .

#### MANGANESE AND CHLORINE.

a. Protochloride of Manganese.  $\text{MnCl} = 63.1$ .

This salt is best obtained by the following process:—The solution formed in the preparation of chlorine by means of peroxide of manganese and hydrochloric acid, which is generally a mixture of chloride of manganese and more or less perchloride of iron, is first rendered neutral by gently evaporating it to dryness. It is then redissolved, and a portion of it precipitated by carbonate of soda, which throws down a mixture of peroxide of iron and carbonate of manganese.  $\text{MnCl} + \text{FeCl}$  acted on by  $4(\text{NaO}, \text{CO}_2)$  yield  $(\text{MnO}, \text{CO}_2) + \text{Fe}_2\text{O}_3 + 4\text{NaCl} + 3\text{CO}_2$ . The precipitate is well washed, and then boiled with the rest of the solution, when the oxide of manganese in the precipitate acts on the perchloride of iron in the solution, producing chloride of manganese, which dissolves, and peroxide of iron, which separates  $3(\text{MnO}, \text{CO}_2) + \text{Fe}_2\text{Cl}_3 = 3\text{MnCl} + \text{Fe}_2\text{O}_3 + 3\text{CO}_2$ . The filtered liquid is free from iron, if we have hit the proportion right; if not, a second operation with a smaller portion of

the liquid will complete the purification. The pure solution is evaporated to dryness in a retort, and there fused. On cooling, the protochloride forms a pink crystalline mass. Iron is the ordinary impurity to be removed; but if other metals be present, they are to be got rid of by appropriate means. Thus, if cobalt and nickel are present, which they generally are in small quantity, the addition of hydrosulphuret of ammonia, as long as it causes a dark precipitate, or till it produces the pure flesh colour characteristic of manganese, will remove them. The chloride of manganese is used for preparing, by the action of an alkaline carbonate, pure carbonate of manganese, from which all other salts of manganese may be obtained.

A sesquichloride of manganese is said to be formed when hydrochloric acid acts on the sesquioxide in the cold. It is little known.

b. Perchloride of Manganese.  $\text{Mn}_2\text{Cl}_7 = 303\cdot7$ .

This compound, which corresponds to the permanganic acid, is formed, according to Dumas and Wöhler, when permanganate of potash is heated along with common salt and sulphuric acid.  $\text{KO}, \text{Mn}_2\text{O}_7 + 7\text{NaCl} + 8\text{SO}_3 = \text{KO}, \text{SO}_3 + 7(\text{NaO}, \text{SO}_3) + \text{Mn}_2\text{Cl}_7$ . It is a greenish-brown volatile liquid, which is instantly decomposed by contact with moist air, forming a dense cloud of a pink colour. Here water is acted on, and the products are hydrochloric and permanganic acids.  $\text{Mn}_2\text{Cl}_7 + 7\text{HO} = \text{Mn}_2\text{O}_7 + 7\text{HCl}$ . It is probable, however, that this volatile liquid may be an oxychloride, analogous to that of chromium.

c. Perfluoride of Manganese.  $\text{Mn}_2\text{F}_7 = 187\cdot5$ .

When mineral chameleon (or better, permanganate of potash) is acted on by sulphuric acid and fluoride of calcium (fluor spar) with the aid of heat, a greenish-yellow gas or vapour is disengaged, which, with moist air, instantly becomes red. It acts powerfully on glass. Its composition seems to correspond to that of the preceding compound, and its production is to be explained in the same way, substituting fluoride of calcium for chloride of sodium. (Wöhler.) But it may be an oxyfluoride.

d. Protosulphuret of Manganese.  $\text{MnS} = 43\cdot6$ .

This compound is found native. It may be formed by passing a current of sulphuretted hydrogen over sulphate of manganese at a red-heat. The sulphuric acid of the sulphate is expelled, and the protoxide is acted on by the sulphuretted hydrogen.  $\text{MnO} + \text{HS} = \text{MnS} + \text{HO}$ . It is nearly black in colour, and dissolves readily in dilute hydrochloric and other acids, with

disengagement of sulphuretted hydrogen.  $\text{MnS} + \text{HCl} = \text{MnCl} + \text{HS}$ . The flesh-coloured precipitate formed in salts of protoxide of manganese by hydrosulphuret of ammonia, or any other soluble sulphuret, is a hydrated protosulphuret of manganese,  $\text{MnS}$ ,  $\text{HO}$ .

#### 27. IRON. $\text{Fe} = 28$ .

This important and useful metal occurs very abundantly in nature. It is occasionally found in the uncombined state in masses, most probably of meteoric origin, which always contain traces of cobalt and nickel, and very often sulphur and arsenic; sometimes, it is said, chromium. Though very hard, meteoric iron is malleable, but its most common form is that of oxide, frequently uncombined, frequently also combined with carbonic acid. It is found, likewise, abundantly as sulphuret. There is hardly a rock, a soil, or a mineral which does not contain more or less of oxide of iron: and the carbonate is a frequent ingredient in mineral waters, which are then termed chalybeate waters.

The chief ores of iron are—1. Clay iron stone, which is a more or less pure carbonate of protoxide, generally containing carbonates of lime and magnesia; it accompanies coal beds both in England and in Scotland. 2. Red hematite, which is pure peroxide or sesquioxide of iron; and brown hematite, which is hydrated peroxide. 3. Black or magnetic oxide of iron. Less abundant ores are, specular iron ore, or crystallised anhydrous peroxide; spathic iron ore, or crystallised carbonate of protoxide; black band, a variety of the compact carbonate or clay iron-stone, containing bituminous matter; and bog iron ore, a mixture of hydrated peroxide and phosphate of iron in variable proportion. Iron pyrites, the bisulphuret, is used to supply sulphur, but not as an ore of iron, as it yields a very inferior quality of metal.

From its ores iron is obtained by heating them in blast furnaces, in the upper part of which the ores are stratified with coal, lime, and sandstone. The carbon of the coal, at a red-heat, reduces the iron to the state of metal, while the sand and lime act as a flux, and form a liquid slag, through which the melted iron falls to the lower part of the furnace, where it is drawn off. The slag is drawn off above the iron, and on cooling is found to be a mixture of silicates of lime and magnesia with a little iron.

The process of smelting iron has been of late wonderfully improved by the use of the hot blast, that is, by supplying the blast furnaces with the necessary current of air, which is always forced

in at the lower part of the furnace, not, as formerly, cold, by which the furnace was cooled, and much heat lost, but at a temperature of  $600^{\circ}$ . This heat may be procured by burning the combustible gases which fill the upper part of the furnace. The saving effected is so great, that whereas, with the cold blast, 8 tons of fuel were required to yield 1 ton of iron, with the hot blast  $2\frac{3}{4}$  tons of fuel produce the same quantity. This diminution of bulk also enables the iron master to smelt more iron ore in the same time. He is also enabled to use coal, instead of previously coking it, as was formerly necessary. The iron from the hot blast is slightly inferior in quality to cold blast iron, but means have been found to remedy this defect, and the hot blast, in Scotland for example, is now universally employed. In 1851, 2,500,000 tons of iron were produced in Great Britain.

The iron thus obtained, which is called pig iron or cast iron, is not pure, containing some unreduced ore, or earthy matters, and a good deal of combined carbon. It is far more fusible than pure iron, but also far more brittle. To convert it into pure or malleable iron it is melted and exposed to a current of air, which gradually burns off the carbon. The mass is well stirred, and the other impurities rise to the surface as slag or dross. By degrees the metal becomes less fusible, and the heat must be increased, till, at last, with the strongest heat, the metal continues solid. It is then well hammered while hot, by which it is still further purified, and rendered more dense. It is not yet absolutely pure, containing about.  $\frac{1}{2}$  per cent. of carbon and a trace of silicon. A very good test of the purity of iron is its ductility. Unless very pure, it cannot be drawn out into fine wire.

If perfectly pure iron is wanted, the filings of malleable iron should be fused with  $\frac{1}{4}$  their weight of black oxide of iron, and some green glass to act as a flux. Or pure oxide of iron may be reduced to the metallic state by passing a current of hydrogen gas over it at a red heat. The metal remains as a gray powder, which, if reduced at a low heat, takes fire, burning like tinder in the air. If reduced at a strong red heat it is permanent.

Pure iron has a gray colour, and strong lustre when polished. It is very ductile, moderately malleable, and remarkably tenacious. It is hard at common temperatures, but at a red-heat it is so soft that it may be beaten into any form, and even admits of being welded; that is, two pieces of iron being heated red-hot, may be, by hammering, so incorporated into one, that no joining is perceptible. Its Sp. G. is 7.7. It is very infusible, requiring the very highest temperature of a wind furnace to melt it.

Iron is attracted by the magnet, and may, in the form of steel, be rendered permanently magnetic by various means.

The attraction of iron for oxygen is very powerful, and when exposed to air and moisture it rusts rapidly, forming oxide of iron. When heated to redness in air, iron is very quickly covered with a crust of black oxide, which scales off under the hammer. If heated to redness in oxygen, or to whiteness in the air, it burns with vivid scintillations. To secure the result in the air, the white hot metal must be exposed to a current of air from a bellows, or rapidly whirled round. Iron decomposes water rapidly at a red-heat.

#### IRON AND OXYGEN.

##### a. Protoxide of Iron. $\text{FeO} = 36$ .

This oxide is a powerful base, almost unknown in a separate state, owing to its tendency to attract an additional quantity of oxygen. It combines with acids, forming salts, which have generally a pale bluish-green colour, although some are colourless. Several of these salts are of great importance in medicine and in the arts, particularly the sulphate of iron, or green vitriol.

The solutions of these salts give with alkalies, when no trace of peroxide is present, a bulky white precipitate of hydrated protoxide of iron, which soon becomes green, and lastly brown, being converted into peroxide by absorbing oxygen from the air. They give a similar precipitate, not more permanent, with carbonated alkalies, which at first is hydrated carbonate of protoxide, but as oxygen is absorbed the carbonic acid is given off, peroxide of iron having no affinity for that acid. With ferrocyanide of potassium they give a pale blue, or rather a white precipitate, which gradually becomes dark blue, and with ferridcyanide of potassium (red prussiate) a deep blue precipitate of Prussian blue. These salts are not affected by sulphuretted hydrogen, sulphocyanide of potassium, meconic acid, or gallic acid. Hydrosulphuret of ammonia, and soluble sulphurets, produce a black precipitate of sulphuret of iron.

The salts of protoxide of iron, for the most part, attract oxygen from the air and from other bodies, passing into salts of the peroxide. Hence they act in some cases as deoxidising agents. Gold is completely reduced from its solutions by protosulphate of iron.

##### b. Sesquioxide of Iron. $\text{Fe}_2\text{O}_3 = 80$ .

*SYN. Peroxide of Iron.*—This oxide is found native, as red

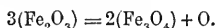
hematite and specular iron ore, and hydrated, as brown hematite. It may be prepared artificially by calcining pure, dried green vitriol, when the protoxide is oxidised at the expense of the sulphuric acid, and water, along with sulphuric and sulphurous acids, is expelled.  $2(\text{FeO}, \text{HO}, \text{SO}_3) = \text{Fe}_2\text{O}_3 + 2\text{HO} + \text{SO}_2 + \text{SO}_3$ . A red powder is left, which is peroxide of iron, and in this form it is used for polishing plate, as jeweller's rouge, or colcothar of vitriol. Hydrated peroxide of iron is obtained by precipitating a solution of persulphate of iron or perchloride of iron by an alkali, whether caustic or carbonated. When protosulphate of iron is precipitated by an alkaline carbonate, the precipitated protocarbonate, during the process of washing and drying, loses its carbonic acid, and attracts oxygen, becoming hydrated peroxide. This, when dry, is a brown powder, used in medicine under the erroneous name of carbonate of iron. In the moist state it is the only known antidote to arsenious acid.

Peroxide of iron is not magnetic. It is a base, although not a powerful one, forming, with acids, salts which are either yellow, brown, or red. The solutions of such salts or persalts of iron, as they are called, are very easily recognised. They give, with caustic or carbonated alkalies, a brown precipitate of hydrated peroxide; with ferrocyanide of potassium a deep Prussian blue: with ferridcyanide of potassium no precipitate, only a dark greenish colour is given to the liquid; with sulphocyanide of potassium, or with meconic acid, a blood-red colour; and with tannic acid (or tannine) and gallic acid, a bluish-black colour (ink). Sulphuretted hydrogen causes a white precipitate of sulphur, while the peroxide is reduced to protoxide; hydrosulphuret of ammonia causes a black precipitate of sulphuret of iron. These tests are so delicate and so uniform, especially those of ferrocyanide of potassium, sulphocyanide of potassium and tannic acid, or infusion of galls, that it is always best, in testing for iron, to convert any protoxide that may be present into peroxide, which is easily done by boiling the solution with a little nitric acid.

c. Magnetic oxides of Iron.  $\text{Fe}_3\text{O}_4 = 116$ : and  $\text{Fe}_4\text{O}_5 = 152$ .

The first oxide is the native magnet, or loadstone, which is a heavy black mineral, strongly attracting iron filings, or steel. It is believed to be composed of protoxide and peroxide, and the native magnet is generally supposed to be  $\text{Fe}_3\text{O}_4 = \text{FeO} + \text{Fe}_2\text{O}_3$ . There is reason, however, to believe that another kind of magnetic oxide exists, which is  $\text{Fe}_4\text{O}_5 = 2\text{FeO} + \text{Fe}_2\text{O}_3$ . At all events, both of these compounds may be formed artificially, and both are magnetic as well as permanent; not absorbing

oxygen, or passing into peroxide. To prepare the former, take 2 parts of green vitriol ; dissolve it in water and convert it into persulphate by boiling with nitric acid ; then mix the solution with the solution of 1 part of the unaltered green vitriol, and precipitate the hot liquid by ammonia. A dark green precipitate falls, which is to be washed and dried. The second magnetic oxide is prepared in the same way, only converting into persulphate 1 part of green vitriol instead of 2 parts. The precipitate is black, if made in the liquid while hot. It is evident that in the latter case the quantity of iron, in the forms of protoxide and of peroxide, will be equal ; in the former, the quantity of iron in the peroxide will be double that in the protoxide, so as to yield the above formulæ. Magnetic oxide of iron is also formed when iron is heated red-hot and hammered. The black scales which separate (smithy ashes) are magnetic. The same oxide is produced when the vapour of water is passed over iron at a red-heat, hydrogen being disengaged, and, according to the recent experiments of Ashby, when finely divided sesquioxide of iron, heated red-hot, is plunged into the strongest liquid ammonia or into alcohol, the ammonia (or alcohol) being oxidised in the process : the following equation represents the change :—



The black magnetic oxide thus produced, when moderately heated over the spirit-lamp, becomes incandescent, absorbing oxygen from the air, and passing into sesquioxide. It is used in medicine.

When black oxide of iron is dissolved in acids, both protoxide and peroxide are present. The latter may be precipitated by digestion with carbonate of lime, after which the former can be detected in solution.

#### d. Ferric Acid. $\text{FeO}_3 = 52.$

This acid, corresponding to manganic acid, is also unknown in the separate state. But its salts are rather more permanent. Ferrate of potash is formed when peroxide of iron is heated to redness with nitre, or when the oxide, suspended in a concentrated solution of caustic potash, is acted on by a current of chlorine. In this process the ferrate of potash, being insoluble in strong potash, is deposited in crystalline grains, nearly black, which may be dried on a porous brick. Its solution has a deep purple colour. Like the manganate, it is easily deoxidised, and the solution, left to itself, gives off oxygen, and deposits peroxide of iron.



## IRON AND CHLORINE.

a. Protochloride of Iron.  $\text{FeCl} = 63\cdot5$ .

This compound is formed when dry hydrochloric acid gas is passed over iron heated to redness, hydrogen gas being disengaged.  $\text{Fe} + \text{HCl} = \text{FeCl} + \text{H}$ . It appears as a white crystalline solid, volatile in a very high temperature. It dissolves readily in water, forming a pale green solution, which yields on evaporation crystals of the same colour. These contain 4 eqs. of water of crystallisation. The characters of this solution, its colour, taste, and reactions, are so exactly those of a solution of a salt of protoxide, that there is some reason to conclude that the chloride, in dissolving, decomposes water, forming protoxide of iron and hydrochloric acid. With chloride of ammonium, this chloride forms a double salt, from the solution of which iron may be deposited in a coherent metallic state on various metals by boiling them in it with fragments of zinc.

b. Sesquichloride of Iron.  $\text{Fe}_2\text{Cl}_3 = 162\cdot5$ .

*SYN. Perchloride of Iron : Permuriate of Iron.*—It is formed when chlorine gas is passed over iron heated to a temperature below redness, when it appears as red iridescent scales, volatile at a temperature little beyond  $212^\circ$ , and soluble in water, alcohol, and ether. A solution of the perchloride is easily obtained by dissolving peroxide of iron in hydrochloric acid:  $\text{Fe}_2\text{O}_3 + 3\text{HCl} = \text{Fe}_2\text{Cl}_3 + 3\text{HO}$ . When evaporated to the consistence of syrup, and cooled, it forms red crystals, which contain 6 eqs. of water of crystallisation. When heated, they are partly decomposed, peroxide being formed, and hydrochloric acid passing off, in consequence of the action between perchloride of iron and water. As perchloride of iron is a volcanic product, it is probably in this way that the crystals of peroxide, found in volcanic districts, have been formed. Perchloride of iron is much used in medicine.

## IRON AND IODINE.

a. Protoiodide of Iron.  $\text{FeI} = 155\cdot1$ .

When iron filings and iodine, in atomic proportions, are brought in contact under water, they rapidly combine, with considerable heat, and the resulting iodide dissolves in the water. The whole is boiled with a slight excess of iron for a short time, and the pale-green filtered solution rapidly boiled down in a Florence flask, till on cooling, it becomes solid. The solid mass

of iodide is broken up, and kept in very closely-stopped bottles. It forms a dark-gray crystalline mass, which is very soluble in water, and forms a pale-green solution; the solution, which is much used in medicine, attracts oxygen rapidly from the atmosphere, and is decomposed, iodine escaping, and peroxide being deposited. It is, therefore, necessary to prepare it extemporaneously, or to keep it in small tightly-corked bottles, with a portion of clean iron wire in each.

b. Periodide of Iron.  $\text{Fe}_2\text{I}_3 = 437.5$ .

This compound is made by causing an excess of iodine to act on iron wire, and subliming the dry mass left after gently evaporating to dryness. It is a volatile, deliquescent body, of a red colour, soluble in water and alcohol.

The bromides of iron are analogous to the chlorides and iodides; and the fluorides correspond in composition, but are sparingly soluble in water.

#### IRON AND SULPHUR.

a. Protosulphuret of Iron.  $\text{FeS} = 44$ .

This sulphuret is prepared by heating iron filings with sulphur in atomic proportions, when they combine with evolution of heat and light. Or a bar of iron may be heated to redness in a forge, and a stick of roll sulphur applied to the hot metal, which is instantly perforated, while the sulphuret falls to the ground in melted globules, having a yellowish colour and metallic lustre. Prepared by the first process, it is partly in crystalline grains, partly in the form of a black powder. It is used for procuring sulphuretted hydrogen gas, which is formed when the protosulphuret is dissolved in hydrochloric or sulphuric acid.  $\text{FeS} + \text{HCl} = \text{FeCl} + \text{HS}$ .

b. Sesquisulphuret of Iron.  $\text{Fe}_2\text{S}_3 = 104$ .

It is formed by the action of hydrosulphuric acid (sulphuretted hydrogen) on peroxide of iron, at a heat not above  $212^\circ$ , as a yellowish-grey powder; or by adding perchloride of iron to an excess of hydrosulphuret of ammonia, as a black powder, rapidly oxidised by exposure to the air.

c. Bisulphuret of Iron.  $\text{FeS}_2 = 60$ .

**SYN. Iron Pyrites.**—This is a very abundant mineral, of a yellow colour and metallic lustre, crystallising in cubes or octohedrons. When heated in close vessels, it loses nearly half its sulphur, which may be collected, magnetic pyrites being left.

Iron pyrites is often contaminated with arsenic, which accompanies the sulphur, and is found in the sulphuric acid made from it.

d. Magnetic Pyrites.  $(6\text{FeS} + \text{FeS}_2) = \text{Fe}_7\text{S}_8 = 324$ .

This also occurs in nature, and is attracted by the magnet. It dissolves in acids, yielding sulphuretted hydrogen and a residue of sulphur. Another variety of magnetic pyrites is  $(2\text{FeS} + \text{FeS}_2) = \text{Fe}_3\text{S}_4 = 148$ .

Arfwedson has formed two other sulphurets, the tetrasulphuret,  $\text{Fe}_4\text{S}$ , and the disulphuret,  $\text{Fe}_2\text{S}$ , which have no particular interest. Pyrites yields an inferior iron, from the presence of sulphur in the metal. Even 0.0004 per cent. of sulphur renders iron "hot short," that is, brittle at a red heat.

Diphosphuret of iron is an ingredient in some kinds of iron, and has the bad effect of rendering it "cold short," that is, brittle at common temperatures.

#### IRON AND CARBON.

Iron forms with carbon two distinct compounds, the precise composition of which is unknown. These are cast-iron and steel.

Cast-iron is obtained in the process for extracting iron from its ores. It occurs in two forms, white and grey. Both fuse far more readily than pure iron. White cast-iron is very hard and brittle; it contains from 3 to 5 per cent. of carbon. Grey cast-iron is softer and tougher; it contains between 3 and 4 per cent. of carbon, in part uncombined. A compound of the formula  $\text{Fe}_4\text{C}$ , would contain about 5 per cent. carbon. This is the largest amount with which iron can be made to combine.

Steel contains from 1.3 to 1.75 per cent. of carbon. It is less fusible than cast-iron, and is much harder, more elastic, and more sonorous than pure iron. It is made by cementation: that is, alternate layers of iron and charcoal are placed in a closed chamber and heated to redness for several days, during which time a gradual combination takes place.

In this process, the carbon is conveyed from particle to particle to the very centre. Steel is improved, and rendered more uniform by being cast. A uniform and good steel is also obtained by heating iron in coal gas. Steel is rendered singularly hard, elastic, and brittle, by heating it to redness, and plunging it into cold water, oil, or mercury. To remove the extreme brittleness and hardness, so as to adapt it for cutlery of various kinds, it must now be annealed, that is, heated to

various points, according to the object in view, and then slowly cooled. The temperature to which it is heated is judged of by the colours of the film of oxide formed on the surface, which is, with a heat of about  $430^{\circ}$  to  $450^{\circ}$ , a light straw-colour; this is suited for razors and surgical instruments, being the hardest tempered steel: at  $470^{\circ}$  the colour is a strong yellow, suited for pen-knives and fine cutlery; at  $490^{\circ}$  it is a brownish-yellow, fit for shears for cutting iron; at  $510^{\circ}$  purple begins to appear; this steel is used for garden and pruning-knives;  $520^{\circ}$  gives a purple; the steel is fit for table and carving knives; and from  $530^{\circ}$  to  $570^{\circ}$  shades of blue are produced, the steel being very elastic and used for saws, sword-blades and watch-springs.

#### 28. ZINC. $Zn = 32.6$ .

This metal is found in considerable abundance. It occurs, as sulphuret, in zinc blende; and as carbonate of the oxide in calamine; also as red oxide, which is oxide of zinc, coloured by oxides of iron and manganese. As calamine often contains silicate of zinc, the zinc in that form is not obtained, and is therefore lost. To obtain the metal, the sulphuret is roasted in the air until the sulphur is burnt off, and the zinc converted into oxide; or, what is preferable, the carbonate is heated till all the carbonic acid and water it contains are expelled, leaving oxide of zinc. The oxide is now mixed with charcoal and the mixture distilled in retorts, or in crucibles, closed at the top, but having a tube open at both ends fitted into the bottom, and reaching, within, nearly to the cover. The oxide is reduced by the action of the charcoal at a full red-heat, and the metal being volatile, distils over and is condensed in vessels of sheet iron.

Zinc has a bluish-white colour and bright lustre, and tarnishes slowly on exposure to the air. Its Sp. G. is about 7. It is brittle at ordinary temperatures; but between  $200^{\circ}$  and  $300^{\circ}$ , it is both malleable and ductile, and may be rolled or hammered into sheets of considerable thinness. It melts at  $773^{\circ}$  (Daniel), and at a high-red or white-heat sublimes or distils unchanged in close vessels. Heated strongly in air, it takes fire and burns with a beautiful greenish-white light, forming oxide of zinc, which may be thus formed in large quantity, if the burning metal be well stirred, so as to expose it to the air. A certain proportion of the oxide is carried up by the current of hot air, and is deposited in light flocculent masses, formerly called *lana philosophorum*.

## ZINC AND OXYGEN.

Protoxide of Zinc.  $\text{ZnO} = 40\cdot6$ .

The oxide which is formed when zinc is burned in the air is the only compound of these elements. It is purified from unoxidised metal by levigation and elutriation with water. It may also be obtained by heating the carbonate to redness, or by precipitating the sulphate of zinc by a caustic alkali, in which latter case we obtain a bulky gelatinous hydrate of the oxide. Oxide of zinc is a fine white powder, which becomes yellow when strongly heated, but on cooling recovers its whiteness. It is insoluble in water, but very soluble in acids, which it neutralises, being a very powerful base, of the same class as magnesia.

Solutions of oxide of zinc are recognised by the following characters. Caustic alkalies produce a bulky white precipitate of hydrate, soluble in an excess of the alkali. The alkaline carbonates precipitate a bulky white carbonate of zinc, permanent when carbonate of soda or potash is employed, but soluble in excess of carbonate of ammonia. Sulphuretted hydrogen has no action if the solution be strongly acid; but if it be neutral forms a white precipitate of hydrated sulphuret of zinc, which is best formed by hydrosulphuret of ammonia. Ferrocyanide of potassium also causes a white precipitate.

Chloride of Zinc.  $\text{ZnCl} = 68\cdot1$ .

This compound is formed by the action of chlorine on zinc, or by dissolving zinc in hydrochloric acid, when hydrogen is evolved.  $\text{Zn} + \text{HCl} = \text{ZnCl} + \text{H}$ . The solution is evaporated to dryness and sublimed in a current of hydrochloric acid gas. It is white, semi-solid, very fusible, volatile at a red-heat, and highly deliquescent. It was formerly called butter of zinc. Chloride of zinc absorbs ammonia, and forms double salts with the alkaline chlorides. That with chloride of ammonium,  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}$ , is used in soldering, to clean the surfaces of metals by dissolving the films of oxide which form. Chloride of zinc is used in organic researches, to deprive certain compounds of the elements of water, for which it has a very strong attraction. Its solution is a very powerful antiseptic, and is used to preserve anatomical subjects and preparations. It is also employed as a mild caustic in surgery.

Iodide of Zinc.  $\text{ZnI} = 159\cdot7$ .

When iodine is acted on by excess of zinc under water, an energetic combination takes place, and a colourless solution

is obtained which, on evaporation, leaves a deliquescent mass, very analogous to the chloride, and capable of being sublimed in crystals.

The bromide and fluoride of zinc are little known.

Sulphuret of Zinc.  $\text{ZnS} = 48.6$ .

Sulphuret of zinc occurs native, under the name of zinc blende, the most abundant ore of zinc, in dodecahedral crystals, which are sometimes yellow, sometimes red, brown, or black. It may be formed by heating oxide of zinc with sulphur, or sulphate of zinc with charcoal in a closed crucible.  $\text{ZnO}, \text{SO}_3 + \text{C}_4 = 4 \text{CO} + \text{ZnS}$ . When a mixture of zinc and sulphuret of mercury is heated, a violent, almost explosive action takes place, and sulphuret of zinc is formed, while mercury volatilises.

29. CADMIUM.  $\text{Cd} = 56$ .

This metal occurs, in the form of carbonate, as an ingredient in various kinds of calamine or carbonate of zinc. It is also found in the form of sulphuret, as the rare mineral greenockite, in fine orange-yellow transparent octohedrons; and to the extent of 5 per cent. in some kinds of sulphuret of zinc. The metal is, in all its relations, very analogous to zinc, and is almost invariably found associated with it.

When an ore of zinc, containing cadmium, is treated as above described, to obtain the zinc, the first vapours that distil over, which are known as the brown blaze, contain the cadmium, and are separately collected. To purify it from zinc, it is dissolved in an acid, and the solution acted on by a piece of zinc in a platinum vessel. The cadmium is reduced, and adheres to the platinum, the zinc being dissolved in its place. When well washed, the cadmium may be dissolved off by nitric acid. On the acid solution of both metals may be precipitated by sulphuretted hydrogen, which throws down cadmium and not zinc. The sulphuret of cadmium is then dissolved in nitric acid. From this solution alkalies throw down oxide of cadmium, which is reduced exactly like oxide of zinc.

Cadmium is in appearance similar to tin, but is more tenacious. It is so soft, that, like lead, it makes a mark on paper. A rod of it, when bent, creaks like a rod of tin. It is both malleable and ductile. Its Sp. G. is 8.6. It melts below red heat, forming octohedral crystals on cooling, and boils at a temperature not a great deal higher than the boiling point of mercury. When strongly heated in the air, it burns, forming oxide. Like zinc, it forms only one oxide, chloride, sulphuret, &c.

Oxide of Cadmium.  $\text{CdO} = 64$ .

The oxide is best prepared by heating the carbonate to redness. It is an insoluble orange powder, which is a strong base, neutralising acids. Its salts are easily recognised by the following tests. Caustic alkalis cause a white, bulky precipitate of hydrated oxide, which dissolves in excess of ammonia. Sulphuretted hydrogen produces an orange precipitate of sulphuret of cadmium.

The chloride and iodide of cadmium are white fusible compounds.

The sulphuret of cadmium, as precipitated from solutions of the metal by sulphuretted hydrogen, is an orange-yellow powder, soluble in nitric acid, and distinguished from yellow sulphuret of arsenic by being insoluble in ammonia and caustic potash, as well as in the alkaline sulphurets, and fixed in the fire. It is found native, in orange-yellow transparent octohedrons, called greenockite.

The sulphate of cadmium is used as a collyrium, and internally is a powerful emetic, even in very small doses.

30. TIN.  $\text{Sn} = 59$ .

This important metal occurs in Cornwall, in Saxony, in Sweden, and in the East, in the form of oxide, from which the metal is obtained by heating with charcoal. This, the only valuable ore of tin, or tinstone, as it is called, occurs in veins in primitive rocks, with the sulphides and arseniurets of copper and iron, in the form of heavy brown prisms. It is associated with albite or soda felspar, topaz or pycnite, and lithion-mica. It is the deutoxide or stannic acid,  $\text{SnO}_2$ . This mineral is also found in small rolled fragments, in alluvial beds in tin districts; it is then called stream tin.

Tin is a white metal, with a very high lustre, which is very little tarnished by exposure to the atmosphere. It is very malleable, yielding leaves (tinfoil) not thicker than  $\frac{1}{1000}$  of an inch. It is soft, and when bent in the fingers makes a peculiar noise. Its Sp. G. is 7.2. It melts at  $442^\circ$ , and if heated to whiteness in air, it takes fire and burns with a white flame, forming peroxide of tin.

From its lustre and its small tendency to tarnish in air, tin is much used as a coating on the surface of other metals, such as iron and copper. Tinned iron, often called tin-plate, is made by immersing plates of the best iron, carefully cleaned on the surface, in melted tin. An alloy is formed at the surface of the

iron, but the outer layer is pure tin. Copper is tinned in a manner somewhat analogous.

Tin is also very much used in forming various alloys, of which the most valuable are: Britannia metal, composed of equal parts of brass, tin, bismuth, and antimony; pewter, which consists chiefly of tin and lead: the best contains 4 parts of tin to 1 of lead. Queen's metal contains tin, with a little antimony, lead, and bismuth. Soft solder is formed of lead and tin, in various proportions, according to the fusibility required. With copper, in different proportions, tin forms bell metal and gun metal. Bronze contains copper, with tin and zinc; and speculum metal contains more tin than any of the other alloys with copper, namely, 1 part of tin to 2 of copper, which corresponds to a definite formula,  $\text{SnCu}_4$ . The amalgam of tin with mercury is used for the silvering of mirrors.

#### TIN AND OXYGEN.

##### a. Protoxide of Tin. $\text{SnO} = 67$ .

This oxide is prepared by adding an alkaline carbonate to a solution of protochloride of tin, when a bulky white precipitate is formed of hydrated protoxide of tin. This is washed with warm water and dried at a heat not above  $196^\circ$ . The dry hydrate is now heated to redness in a current of carbonic acid gas, and the anhydrous protoxide is left.

Protoxide of tin is a dense black powder, which has so strong an attraction for oxygen, that if touched with a red-hot body it takes fire and burns into peroxide. It dissolves in acids forming salts which absorb oxygen with avidity, and reduce the oxides of silver, mercury, and platinum to the metallic state if added to their solutions. With solutions of gold, salts of protoxide of tin produce a purple precipitate, the purple of Cassius, so that salts of gold and salts of protoxide of tin are mutually tests for each other. Salts of protoxide of tin give, with sulphuretted hydrogen, a brown precipitate of protosulphuret of tin.

##### b. Sesquioxide of Tin. $\text{Sn}_2\text{O}_3 = 142$ .

When moist hydrated peroxide of iron is mixed with a neutral solution of protochloride of tin, an exchange takes place, and a bulky precipitate of a grey colour is formed, which is a hydrate of sesquioxide of tin.  $\text{Fe}_2\text{O}_3 + 2\text{SnCl} = \text{Sn}_2\text{O}_3 + 2\text{FeCl}$ . The sesquioxide is soluble in acids and in ammonia, the latter character distinguishing it from the protoxide. Its solution in hydrochloric acid forms, with chloride of gold, the purple of



Cassius ; and seems, indeed, better adapted for making it than the protoxide. The sesquioxide is most probably the stannate of the protoxide,  $\text{Sn}_2\text{O}_3 = \text{SnO} + \text{SnO}_2$ .

c. Stannic Acid.  $\text{SnO}_2 = 75$ .

SYN. *Peroxide of tin*.—This oxide is the ore of tin, and, when hydrated, exists in two distinct modifications. 1. If made by the action of nitric acid on tin, which is very violent, it appears as a dense white opaque powder, which is a hydrate, insoluble in water or acids. The formula of this modification is  $5\text{SnO}_2 + 5\text{HO}$ , or more correctly  $\text{Sn}_5\text{O}_{10}, 5\text{HO}$ ; and it is called metastannic acid. It forms salts with bases, that with potash being  $\text{Sn}_5\text{O}_{10} \left. \begin{smallmatrix} \text{KO} \\ 4\text{HO} \end{smallmatrix} \right\}$ . When the hydrated acid is moistened with protochloride of tin a golden yellow metastannate of tin is formed, which is  $\text{Sn}_5\text{O}_{10} + \left. \begin{smallmatrix} \text{SnO} \\ 4\text{HO} \end{smallmatrix} \right\}$ . Metastannic acid is insoluble in nitric or hydrochloric acid; oil of vitriol dissolves it freely with the aid of heat. 2. If prepared by adding potash to perchloride of tin, it forms a very bulky hydrate, readily soluble in acids and also in alkalies. This is hydrated stannic acid,  $\text{SnO}_2, \text{HO}$ . It dissolves in hydrochloric acid, forming bichloride, and yields soluble crystallisable salts, with the alkalies. Stannate of potash is  $\text{KO}, \text{SnO}_2 + 4 \text{ aq.}$  It is recognised in its solution in acids, by forming with alkalies a bulky white hydrate, readily dissolved by excess of potash or soda, and by yielding, with sulphuretted hydrogen, a dirty yellow precipitate of bisulphuret of tin. When melted with glass, peroxide of tin renders it opaque, forming a white enamel. Stannate of soda is now much used in dyeing and calico printing as a mordant.

TIN AND CHLORINE.

a. Protochloride of Tin.  $\text{SnCl} = 94.5$ .

This chloride is formed when hydrochloric acid gas is passed over metallic tin moderately heated, when hydrogen is given off. When dry it is a grey solid, fusible below redness. Tin dissolves in hydrochloric acid, and the concentrated solution deposits acicular crystals, which are a hydrated chloride,  $\text{SnCl} + 3\text{HO}$ . When heated, they give off water and hydrochloric acid, while protoxide is left:  $\text{SnCl} + 3\text{HO} = \text{SnO} + \text{HCl} + 2\text{HO}$ . The addition of a large quantity of water decomposes these crystals, causing the formation of an insoluble white powder, which is a compound of oxide and chloride with water.

The solution of protochloride of tin, made by digesting an excess of tin in hydrochloric acid as long as hydrogen is given off, is much used as a deoxidising agent. It is apparently resolved into bichloride and metal,  $2 \text{SnCl} = \text{SnCl}_2 + \text{Sn}$ ; and the latter, probably, is the true agent in deoxidising. It is also used for making the purple of Cassius. Hydrated protochloride of tin is extensively used as a mordant in dyeing and calico-printing, under the name of salts of tin. It is also used in these arts for deoxidising indigo and the peroxides of iron and manganese.

b. Perchloride of Tin.  $\text{SnCl}_2 = 130$ .

When protochloride of tin is heated in excess of chlorine gas, or when 8 parts of tin powder are distilled with 24 of bichloride of mercury, a volatile fuming liquid is obtained, formerly known as the fuming liquor of Libavius, which is perchloride of tin. It is obtained in solution by dissolving tin in nitrohydrochloric acid of moderate strength, adding small portions of tin at a time; also by forming a solution of protochloride, and passing chlorine through it, or heating it gently with a little nitric acid. It is much used in dyeing as a mordant.

Both the chlorides of tin form crystallisable double salts with the alkaline chlorides. That of the perchloride with chloride of ammonium,  $\text{NH}_4\text{Cl}$ ,  $\text{SnCl}_2$  constitutes the pink salt of the dyer and calico-printer.

The protoiodide of tin is a brownish-red fusible solid, dissolving in water; the periodide forms silky yellow crystals.

TIN AND SULPHUR.

a. Protosulphuret of Tin.  $\text{SnS} = 75$ .

This compound is formed by pouring melted tin on its own weight of sulphur, and stirring well. The mass is then powdered, mixed with more sulphur, and thrown by degrees into a red-hot crucible, by which means the whole of the tin is sulphurised. It forms a bluish-black, brittle solid, having metallic lustre. It is also formed when sulphuretted hydrogen acts on solutions of protoxide or protochloride of tin.

b. Persulphuret of Tin.  $\text{SnS}_2 = 91$ .

This sulphuret, formerly called *aurum musivum*, is prepared by heating to low redness, in a retort, a mixture of two parts peroxide of tin, 2 of sulphur, and 1 of sal-ammoniac. The sulphuret is left in the form of golden-yellow scales, having metallic lustre. It is soluble in potash. It is also formed a

a dirty-yellow bulky hydrate by the action of sulphuretted hydrogen on solutions of peroxide or perchloride of tin. It forms sulphur salts with the alkaline sulphurets. That of sodium,  $2\text{NaS} + \text{SnS}_2 + 12 \text{ aq.}$  forms yellow crystals.

### 31. COBALT. Co = 29.5.

This metal occurs pretty abundantly, generally combined with arsenic, as speiss-cobalt,  $\text{CoAs}$ , or with arsenic and sulphur,  $\text{CoS}_2 + \text{CoAs}$ , as cobalt glance, and associated with nickel and iron; also as sulphuret, and occasionally as sulphate, arseniate, and phosphate. A trace of it is always found in meteoric iron, and generally also in peroxide of manganese. To obtain the metal from the arseniuret, the ore, finely powdered, is gradually added to 3 parts of bisulphate of potash, melted in a moderate heat, and gradually increasing the fire, till no more white fumes appear. The mass, when cold, is powdered and boiled with water as long as anything is dissolved. The solution is free from arsenic, and contains sulphate of protoxide of cobalt. It is precipitated by carbonate of soda, and the washed precipitate acted on by oxalic acid, which forms an insoluble pink powder of oxalate of protoxide of cobalt. Should iron be present, it forms a soluble compound with the oxalic acid, provided it has been brought into the state of peroxide by boiling the solution with a little nitric acid before precipitating with carbonate of soda. The only impurity now likely to be present is nickel, and to separate this, the oxalate is dissolved in an excess of ammonia, and the solution exposed to the air in a deep glass vessel. As the ammonia evaporates, the nickel is deposited (if present) in the form of a pale-green insoluble double oxalate of nickel and ammonia, while the cobalt remains dissolved, forming a port-wine-coloured solution. This being digested with excess of potash, yields a dark-brown precipitate of pure peroxide of cobalt. This is again dissolved in hydrochloric acid, the solution precipitated by caustic potash or carbonate of soda, and the precipitate converted into oxalate, which is now quite pure; and the oxalate being heated to whiteness in a closed crucible, with a small aperture for escape of gas, leaves a button of pure metallic cobalt. The oxalate of cobalt,  $\text{C}_4\text{O}_6, 2\text{CoO}$ , is resolved by the heat into carbonic acid and metal,  $\text{C}_4\text{O}_6, 2\text{CoO} = 4\text{CO}_2 + \text{Co}_2$ .

Cobalt is a metal of a reddish-grey colour, rather brittle and very infusible. Its Sp. G. is 7.8. It is attracted by the magnet. At a red-heat it decomposes water, hydrogen being disengaged.

## COBALT AND OXYGEN.

a. Protoxide of Cobalt.  $\text{CoO} = 37.5$ .

Obtained by calcining carbonate of cobalt in close vessels, as an ash-grey powder. It is a strong base, and forms, with acids, salts which are either pink or blue. Zaffre and smalt, which are so much used for painting blue on porcelain, and by the paper-makers to correct the yellow tinge of their paper, are silicates of this oxide. The solutions of its salts are precipitated by caustic alkalies, which form a blue hydrate, gradually changing to green, soluble in excess of ammonia. Carbonates produce a lilac-coloured precipitate of carbonate of cobalt. Sulphuretted hydrogen produces no change; hydrosulphuret of ammonia produces a black sulphuret. Before the blowpipe, the salts of cobalt give to alumina a fine blue colour. The earth is moistened with a drop of solution of nitrate of cobalt, and this is a delicate test for alumina.

When this oxide, or the peroxide of cobalt, are heated in the air, they both yield a black oxide, which corresponds to the red oxide of manganese, its formula being  $\text{Co}_3\text{O}_4 = \text{CoO} + \text{Co}_2\text{O}_3$ . The green hydrate, formed when hydrate of the protoxide is exposed to the air, is a hydrate of this oxide.

b. Sesquioxide of Cobalt.  $\text{Co}_2\text{O}_3 = 83.0$ .

When bleaching liquor (hypochlorite of lime) is added to solutions of protoxide of cobalt, or when chlorine is passed through hydrated protoxide suspended in water, a black powder is formed, which is hydrated sesquioxide. 3 eqs. of protoxide, and 1 eq. of chlorine, yield 1 eq. of protochloride and 1 eq. of sesquioxide.  $3\text{CoO} + \text{Cl} = \text{Co}_2\text{O}_3 + \text{CoCl}$ .

Sesquioxide of cobalt is, like peroxide of manganese, an indifferent or neutral oxide, for it does not combine with acids; and when dissolved in hydrochloric acid, it forms protochloride, chlorine being disengaged.

It would appear that a deutoxide or peroxide of cobalt exists, although not yet isolated. There has been recently discovered a very remarkable series of compounds containing the elements of ammonia, united to those of different oxides of cobalt; and one series of these compounds appears to contain the oxide  $\text{CoO}_2$ . (Frémy.) It seems probable, that cobalt, with the elements of ammonia, produces various compound basic radicals, which, with oxygen, form bases, and with chlorine, &c., form salts, just as the metals do. The following series have been described, but are not yet fully investigated.

1. Series of oxycobaltia. Formula of the sulphate,  $2\text{CoO}_2, 5\text{NH}_3, 2\text{SO}_3, 3\text{HO}$ . These salts are brown, and when boiled with water, give off oxygen.

2. Series of fuscobaltia. Formula of the sulphate,  $\text{Co}_2\text{O}_3, 2\text{SO}_3, 4\text{NH}_3, 4\text{HO}$ . These salts also are brown. When boiled with acids they yield salts of the next series.

3. Series of roseocobaltia. These are better known than the others. They have a fine rose-red, deep-red, or pink colour, and crystallise readily, being very permanent. Formula of the sulphate,  $\text{Co}_2\text{O}_3, 5\text{NH}_3, 3\text{SO}_3, 3\text{HO}$ . Formula of the hydrochlorate, or chloride,  $\text{Co}_2\text{Cl}_3, 5\text{NH}_3$ . From the sulphate or nitrate, the base may be separated in solution, and appears to be strongly alkaline, but it is not yet known in a state of purity.

4. Series of Luteocobaltia. These salts are orange-yellow, an unexpected colour in compounds of cobalt. Formula of the sulphate,  $\text{Co}_2\text{O}_3, 6\text{NH}_3, 3\text{SO}_3, 4\text{HO}$ . Formula of the chloride,  $\text{Co}_2\text{Cl}_3, 6\text{NH}_3$ . This latter salt forms very fine crystals, nearly of the colour of bichromate of potash. The base of this series may also be separated, but has not yet been studied.

Beside the above, which demand further study, and probably are of a nature analogous to the basic compounds of platinum and ammonia mentioned in the Organic Chemistry, there is a series of salts, in which the elements of ammonia are added to the salts of protoxide of cobalt, but in which it is not known that a new base is formed. Formula of the ammoniated sulphate,  $\text{CoO}, \text{SO}_3, 3\text{NH}_3$ ; of the ammoniated chloride,  $\text{CoCl}, 3\text{NH}_3, 3\text{HO}$ . For our knowledge of all these compounds, we are chiefly indebted to Frémy, but Claudet had previously formed and carefully analysed the salt, called by Frémy hydrochlorate of roseocobaltia.

Chloride of Cobalt.  $\text{CoCl} = 65$ .

Obtained by passing chlorine over heated cobalt, as a lilac coloured anhydrous mass, or as a hydrate, by dissolving cobalt, or any of its oxides, in hydrochloric acid. The solution is pink, and on evaporation yields beautiful red crystals of hydrated chloride, or possibly hydrochlorate of the oxide. When dried by heat, the chloride is of a deep-blue, but is instantly rendered pink by the contact of water. The crystals are either  $\text{CoCl}, \text{HO}$ , or  $\text{CoO}, \text{HCl}$ . When traces are made on paper with a diluted solution of chloride of cobalt, they are invisible when dry; but, when warmed, assume a decided blue colour, which disappears again on cooling, as they again absorb moisture from the air. This is the most beautiful of the sympathetic inks. If iron or nickel be present, the traces appear green instead of blue.

The sulphurets of cobalt are not of much interest. The protosulphuret,  $\text{CoS}$ , is formed when hydrosulphuret of ammonia acts on salts of protoxide of cobalt, as a black precipitate. According to Wöhler, sulphuret of cobalt is easily obtained by fusing the arseniuret of cobalt with 3 parts of pearlash and 3 parts of sulphur. The arsenic forms a soluble compound, and this is removed by water, leaving sulphuret of cobalt as a black powder. This may be dissolved in nitric acid, and the cobalt purified from iron and nickel, as above described. This process for extracting cobalt from its ores would seem to be the best of all.

The compounds of cobalt, when fused with glass, give to it a beautiful blue colour, and their use in painting the blue patterns on china is well known. The finest cobalt blue for painting is made by heating a mixture of 15 parts of alumina with 2 of phosphate of cobalt to redness. Renman's green is a compound of oxide of cobalt with oxide of zinc.

### 32. NICKEL. $\text{Ni} = 29.6$ .

This metal is rather rare; it occurs, like cobalt, chiefly in combination with arsenic, and associated with iron and cobalt. An ore of nickel, lately found in considerable quantity in veins in gneiss near Inverary, consists of the sulphurets of iron, copper, and nickel. It contains 14 or 15 per cent. of nickel, while the common German ore seldom contains more than 5 or 6 per cent., from the presence of stony matter, and it has the advantage of containing much less arsenic. A very good method of extracting it from the arseniuret, or Kupfer nickel,  $\text{NiAs}_2$ , or from speiss, which is an impure arseno-sulphide, is that of Wöhler, which is to fuse the speiss with 3 parts of pearlash and 3 parts of sulphur. The arsenic forms, with the sulphur and potash, a soluble compound, and the nickel forms with the sulphur an insoluble sulphuret. This is well washed with water, and dissolved in nitric acid; and the solution, after any lead, copper, or bismuth that may be present, have been precipitated by a current of sulphuretted hydrogen, is precipitated by caustic or carbonated potash or soda. The washed precipitate is now acted on by an excess of oxalic acid which forms, with the peroxide of iron that is generally present a soluble, and with the oxide of nickel an insoluble oxalate which of course includes any cobalt that the ore may have contained. The oxalate is now dissolved in an excess of ammonia and the solution exposed to the air. As the ammonia escapes the nickel is deposited as an insoluble double oxalate, while the cobalt remains dissolved as a soluble double oxalate of the metallic oxide with ammonia. The nickel salt, being ignited

leaves an oxide, which may be reduced by heating with charcoal, or dissolved in acid, and again converted into oxalate, which this time is free from cobalt, and appears as a pale apple-green powder. The oxalate of nickel, being well washed, dried, and ignited in a closed crucible, with an aperture for the escape of gas, leaves metallic nickel, which, if the heat be very intense, is fused into a button.

Wöhler gives another process, which is said to be preferable to the above. It consists in projecting the finely powdered ore along with 2 parts of nitre and 1 of carbonate of potash, by degrees, into a red-hot crucible, and finally raising the heat for a good while. The arsenic is oxidised, yielding arsenic acid, which unites with the potash, while the nickel is also oxidised, and forms oxide of nickel, which is left undissolved when the mass is lixiviated with water. This oxide is pure, except from cobalt and iron, which must be separated as above. When these metals are not present, the oxide may be at once reduced by heating with charcoal, and yields pure nickel.

These processes are well adapted for operations on the small scale, but as nickel, from its use as an ingredient in German silver, is now in much request, the following process is followed on the large scale. Speiss is first melted with chalk and fluor-spar; the regulus of metal thus obtained is powdered and roasted till the arsenic is expelled. The residue is dissolved in hydrochloric acid, the solution diluted, and the iron peroxidised by the cautious addition of bleaching powder. Milk of lime is now added, so long as peroxide of iron falls, which carries with it the last traces of arsenic. The liquid is now treated with sulphuretted hydrogen, which throws down the sulphurets of copper, lead, and bismuth. The remaining liquid contains only nickel and cobalt; chloride of lime precipitates the cobalt as sesquioxide, and lastly, milk of lime precipitates, from the filtered liquid, the nickel as hydrated protoxide, from which the metal is obtained.

Nickel is nearly silver-white, but has a tinge of grey. It has a high lustre, is hard and malleable. Its Sp. G. is 8·9. It is very infusible, and decidedly magnetic. It decomposes water at a red-heat. Magnetic needles may be made of it, which do not rust. It is now much used in the manufacture of German silver or argentan, which is an alloy of copper, zinc, and nickel. The better qualities contain more nickel than the inferior kinds, and a good proportion is, in 100 parts, about 51 of copper, 30·5 of zinc, and 18·5 of nickel.

## NICKEL AND OXYGEN.

Protoxide of Nickel.  $\text{NiO} = 37.6$ .

Its preparation is given above, in Wöhler's second process for metallic nickel. It is a greenish-grey powder, which is a base, and forms, with acids, salts which are all green, of different shades. Solutions of these salts give pale apple-green precipitates of hydrate and carbonate, with caustic and carbonated potash and soda. Ammonia causes a slight precipitate, which is instantly re-dissolved by an excess, forming a violet-blue solution. Salts of nickel are not precipitated, in acid solutions, by sulphuretted hydrogen, but hydrosulphuret of ammonia causes a black precipitate of sulphuret of nickel.

b. Peroxide of Nickel.  $\text{Ni}_2\text{O}_3 = 83.2$ .

SYN. *Sesquioxide of Nickel*.—May be formed by passing chlorine through water, in which the hydrated protoxide is suspended. It is an indifferent oxide or superoxide analogous to the sesquioxide of cobalt. It is a black powder.

Chloride of Nickel.  $\text{NiCl} = 65.1$ .

Analogous to chloride of cobalt. Its solution is emerald-green, and yields crystals of the same colour; but when entirely deprived of water, it is yellow. At a low red-heat it sublimes and condenses in brilliant gold-yellow scales.

Protosulphuret of Nickel.  $\text{NiS} = 45.6$ .

Analogous to protosulphuret of cobalt, and formed in the same way. Sulphur and nickel unite when heated together, with disengagement of heat and light, forming a greyish-yellow metallic mass. The precipitated sulphuret is black. Sulphuret of nickel is found native in fine crystals of a pale brass colour, as the Haarkies of the Germans.

The sulphate of nickel has of late been used with advantage in small doses, in cases of irritable stomach. Its action on the mucous membrane appears to resemble that of oxide of bismuth or of hydrocyanic acid.

It is proper here to point out the very remarkable analogy between cobalt and nickel, as well as the singular connection which exists between them. All the ores of cobalt contain nickel, while all those of nickel contain cobalt. A similar relation exists between iron and manganese, which are almost invariably found associated together. Even where a mere trace of cobalt occurs, as in the native peroxide of manganese, nickel accom-



panies it ; and in meteoric iron both metals constantly occur. This constant association indicates a remarkable similarity in properties, and in fact we have seen that, colour excepted, the characters and composition of the compounds of nickel are the same as those of cobalt. Nay, they even agree in being magnetic, and as they are found with iron, the only other magnetic metal, in meteoric iron, it is probable that the magnetic character is concerned in the formation of *aërolites*.

ORDER 2.—METALS WHICH DO NOT DECOMPOSE WATER AT ANY TEMPERATURE, AND THE OXIDES OF WHICH ARE NOT REDUCED TO THE METALLIC STATE BY THE SOLE ACTION OF HEAT.

33. ARSENIC.  $As = 75$ .

This metal is occasionally found native, but it is chiefly met with in combination with cobalt, nickel, and iron. When the arseniurets of these metals are heated to redness in a current of air, a great part of the arsenic, being volatile, rises in vapour, and is deposited in the cold part of the chimney in the form of white oxide of arsenic, or arsenious acid, the well-known white arsenic of commerce. This substance is mixed with charcoal or black flux (a mixture of charcoal with carbonate of potash), and the mixture introduced into a medicine phial, filling it about one-third. The phial is then placed in sand, the sand reaching as high as the mixture, and gradually heated to low redness. The metal sublimes and condenses in the upper part of the phial, which, when cold, may be cut off. Arsenic occurs also in the form of arsenic acid combined with the oxides of lead, copper, iron, &c. It is also found united with sulphur, as the red bisulphide, *realgar*, or the yellow tersulphide, *orpiment*.

Arsenic is a very brittle metal, of a whitish-grey colour, and very high lustre. Its sp. g. is 5.80. When heated to  $365^{\circ}$ , it sublimes without previously melting, its melting point being higher than its boiling point under the usual pressure. Its vapour has a strong alliaceous smell, a property which is characteristic of arsenic, no other metal possessing it. It sometimes rapidly tarnishes on exposure to the air, becoming nearly black ; and when heated in a current of air it is oxidised, burning with a blue flame, and being converted into arsenious acid. The rapid tarnishing of arsenic is probably owing to the presence of a little potassium, derived from black flux : for the native metal, when sublimed, does not tarnish.

## ARSENIC AND OXYGEN.

a. Arsenious Acid.  $\text{AsO}_3 = 99$ .

The formation of this substance, when arsenic is sublimed in a current of air, has been mentioned. It occurs, when newly sublimed, as a hard brittle glass, which, when kept, slowly becomes opaque and crystalline, the change often taking years to reach the centre of a small lump of the glass. The sp. g. of arsenious acid is 3.7. At  $380^\circ$  it sublimes, yielding inodorous vapours, which condense in octahedral crystals, when the sublimation is slowly conducted in a glass tube.

It has little taste, which renders it the more dangerous as a poison : as, when taken by mistake, there is no warning, as in the case of many other poisons. It is sparingly soluble in water, but the crystalline variety is more soluble than the glassy ; 100 parts of hot water dissolving 11.5 of the former, and only 9.7 of the latter.

Arsenious acid, whether in the solid form, or in that of solution, is a most virulent poison, and is, unfortunately, so accessible as to be often used for criminal purposes. Its detection, therefore, is a matter of the utmost importance ; and innumerable tests, more or less effectual, have been proposed. These, however, may with advantage be reduced to a very small number ; which again are best divided into—1. Those tests which apply to pure arsenious acid, or its salts ; and, 2. Those which apply to mixtures, such as are likely to occur in medico-legal investigations.

1. Pure arsenious acid is easily recognised, as a heavy white powder, volatile, without smell, sparingly soluble in water, and, when heated with charcoal, black flux, formiate of soda, or cyanide of potassium, yielding a volatile crust of metallic arsenic, the vapours of which have the odour of garlic.

The solution gives, with lime-water in excess, an insoluble white precipitate of arsenite of lime ; with ammoniaco-nitrate of silver, a yellow precipitate of arsenite of silver ; with ammoniaco-sulphate of copper, a grass-green precipitate of arsenite of copper ; and with sulphuretted hydrogen, acetic or hydrochloric acid being first added to the solution, an orange-yellow precipitate of tersulphuret of arsenic. When to the solution of arsenious acid, or of any of its salts, sulphuric acid is added, and a portion of pure zinc introduced into the acid liquid, the hydrogen disengaged by the action of the zinc on the acid is found to be mixed with a portion of arseniuretted hydrogen gas, the presence of which gives it an alliaceous smell, and causes it to burn with a pale blue flame. If a piece of cold glass or

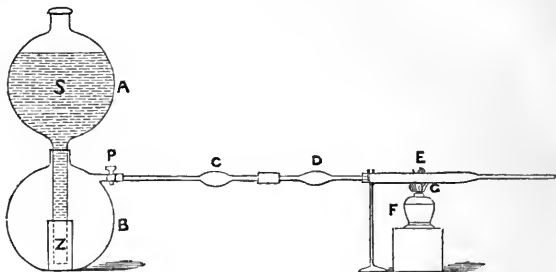
porcelain be held in contact with this flame, a black stain or crust of metallic arsenic is deposited on it, and this crust may easily be recognised by its volatility, and the other characters of arsenic, particularly that of being converted, when gently heated in the tube (open at both ends, and held inclined upwards from the flame, so as to establish a current of air), into arsenious acid, which forms brilliant octohedral crystals, of microscopic size, soluble in boiling water. (Marsh). If the hydrogen gas, containing arseniuretted hydrogen, instead of being burned at the end of the tube, be slowly passed through a long narrow tube of hard glass, part of which is heated to redness, the arseniuretted hydrogen is decomposed at the red-hot part of the tube, and the arsenic deposited in a bright metallic ring a little beyond the hot part.

2. When, however, arsenious acid occurs in mixtures containing much organic matter, such as, for example, are found in the stomach or intestines of those poisoned with arsenic, or in the matters vomited before death, perhaps the best and easiest method is to apply to the mixed fluid the process of Marsh, above noticed. First, however, the liquid, along with any suspected solid matters, is to be boiled with the addition of a little water and a quantity of hydrochloric acid, equal to about  $\frac{1}{10}$ th of the bulk of the liquid and water. It is recommended by some to add also some chlorate of potash. By this means the arsenious acid is dissolved, and it will be found that the liquid when cold does not froth up when hydrogen is formed in it. It may be filtered, but this is not always necessary. It is next introduced into an apparatus where it may act on zinc, so as to produce a rather slow but continuous current of hydrogen. The zinc and acid (hydrochloric acid is preferable to sulphuric) must be first tried alone for an hour, the gas disengaged being made to pass through a narrow tube, heated to redness at one point. If no deposit of arsenic appear in the tube, the suspected liquid, duly acidulated, is introduced, and the experiment continued. Of course any arsenic which now appears cannot have proceeded from the zinc or the acid, and must, therefore, be derived from the suspected matter.

Various forms of apparatus have been proposed, but the best appears to be that used for Dobereiner's lamp, consisting of two globes, the upper having a long tube which fits into the neck of the lower and reaches down to the bottom of it. Round this tube the zinc is rolled, and the gas escapes by a lateral stop-cock in the upper part of the lower globe, being expelled by the pressure of the liquid which is forced into the upper vessel by the gas, till the stop-cock is opened. The gas may be dried

by passing it first through a tube loosely filled with cotton wool, and then through another with chloride of calcium. It then enters the narrow tube of infusible glass, in which it is to be heated to redness at one part.

In the figure, A is the upper globe, B the lower, S the acid liquid, Z the zinc cylinder, P the stop-cock, closed; C the tube with cotton, D that with chloride of calcium, and E the tube in which the gas is heated by the spirit-lamp, F. By regulating

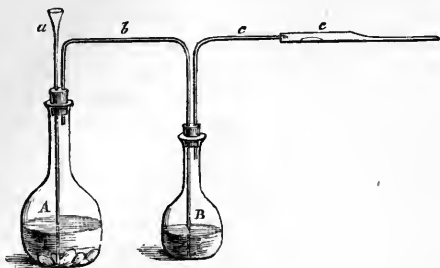


the stop-cock it is easy to regulate the current of gas to the required degree of slowness. By setting fire to it as it escapes at the end of the tube, and holding a piece of porcelain in the flame, it is also easy to ascertain whether any arsenic escapes deposition on the tube at G, just in front of the flame of the lamp.

The simple process above described will be found successful in almost every case. The only difficulty that can arise is from the frothing of the liquid, but this apparently does not take place when the experiment is conducted as above. For the various complicated and tedious processes recommended for the destruction of the organic matter, the reader is referred to the works on toxicology and legal medicine, to which they properly belong. Should antimony be present, which is possible, as it may have been used as an emetic, rings and spots somewhat like those of arsenic, may be formed. But arsenic is easily known by the characters already given, and deposits of antimony dissolve in sulphide of ammonium, and the liquid, when dried up, leaves the brownish-orange tersulphide of antimony. A drop of solution of chloride of lime dissolves arsenic, but not antimony, and finally antimony does not yield the crystals of arsenious acid when heated in a tube.

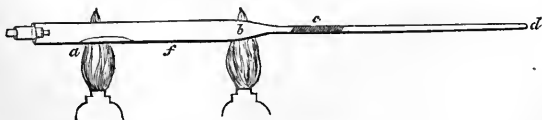
When it is desired to obtain metallic arsenic from a small quantity of the sulphuret, produced in searching for the meta,

it may be best done by heating the dried sulphuret with a reducing agent in a current of carbonic acid gas. This is managed as follows :—



A is a well-sized flask for generating carbonic acid gas, half filled with water and fragments of marble. Through one aperture in the cork passes the funnel tube *a*, reaching nearly to the bottom ; through the other passes a tube *b*, which conducts the gas into the smaller flask B, in which it is washed and dried by passing through oil of vitriol. The tube *c* carries the gas into the reduction tube C, which is represented in the figure below a little less than half the real size.

When the whole is fitted and arranged, a portion of the dried sulphuret (reserving part for other experiments, or in case of accident), is mixed in a warm agate mortar with about twelve parts of a mixture of three parts of dried carbonate of soda and one part of cyanide of potassium. The mixed powder is carefully introduced, by means of a half cylinder of card, into the reduction tube, which is then turned on its axis, so as to allow the powder to lie on the part *a f*, of the reduction tube. The card is then removed. The reduction tube is now attached to the gas apparatus, and hydrochloric acid poured into the flask A, through the funnel, so as to cause a disengagement of carbonic acid gas, which fills the whole apparatus. The tube is then gently warmed through its whole length, until all traces of



moisture have disappeared, and when the current of gas has become so slow that the bubbles follow each other at an interval of about a second, the part *b* of the reduction tube is heated to

redness by a spirit lamp. This being done, the powder is now heated by another spirit lamp from *a* towards *f*, gradually, till all the arsenic is expelled.

The reduced arsenic is deposited as a bright metallic ring at *c*, a mere trace only escaping at *d*. The second lamp is then brought towards *b*, in order to collect any trace of arsenic in the wide part of the tube, and the point *d* being closed by melting it, and the tube detached, the arsenic is driven into as small a space as possible by heating from *d* towards *c*. The tube is now cut across at *f*, corked, sealed, and preserved as evidence. If the above process be followed exactly, the result is a ring of astonishing purity and brilliancy. The use of the carbonic acid is to prevent oxidation by the air, which as well as moisture, if admitted, would very much interfere with the result.

Another delicate test is that of Reinsch, which consists in boiling strips of thin copper plate in the suspected liquid, after it has been acidulated with hydrochloric acid, and boiled with the solid matters. The copper, if arsenic be present, acquires a steel grey colour from the deposition of arsenic on it. The strips of copper, washed with cold water, and dried in a very gentle heat, may now be heated in the closed end of a test tube, when the arsenic is oxidised, and sublimes in the characteristic crystals of arsenious acid.

The only known antidote to arsenious acid is the hydrated peroxide of iron, the ferrugo of the Edin. Pharmacopœia, which should be given in the moist state, mixed with water. When made for this purpose, the precipitated oxide should never be dried, but kept under water; as when once dried, it is far less efficacious. It acts by combining with the arsenious acid forming a compound which is quite insoluble and inert, and is a basic arsenite of sesquioxide of iron,  $\text{Fe}_2\text{O}_3, \text{AsO}_3$ .

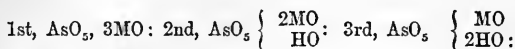
Arsenious acid forms salts, of which that of potash is used in medicine. Arsenite of copper forms a beautiful, but dangerous green colour, Scheele's green. Schweinfurth green is a compound of arsenite and acetate of copper.

#### b. Arsenic Acid. $\text{AsO}_5 = 115$ .

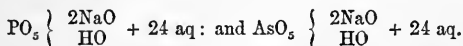
This acid is found in nature combined with oxides of calcium, lead, copper, iron, cobalt, and nickel. It is easily prepared by dissolving arsenious acid in nitric acid, with a little hydrochloric acid, and evaporating to a syrup, which is heated gently till all nitric acid is expelled. The residue is hydrated arsenic acid,  $\text{AsO}_5, 3 \text{HO}$ , or  $\text{AsO}_3, \text{H}_3$ . It is a very acid, poisonous substance, remarkable chiefly for its analogy with common or tribasic phosphoric acid. This analogy is so great, that for

every tribasic phosphate, there is a corresponding arseniate : and this is not all, for the external properties of these salts are so exactly similar, that, except by analysis or characteristic tests, we cannot tell whether arsenic, or phosphoric acid, be present. Not only are the native phosphates of copper, lead, and iron, exactly like the arseniates in colour, crystalline form, and constitution, but the phosphates are seldom found unmixed with arseniates.

The complete isomorphism of arsenic and tribasic phosphoric acids in their salts, is one of the finest examples of isomorphism depending on similarity of constitution. Like the tribasic phosphates, the arseniates occur in 3 forms.



and the crystalline form in all yet examined is the same as that of the corresponding phosphates. Thus the arseniate of soda, with 2 eqs. of soda, and 1 eq. of water, is not to be distinguished, in external aspects, from the common phosphate of soda. The formulæ are—



It is highly probable that phosphorus and arsenic are themselves entirely isomorphous as elements : and in one particular they are alike, besides the analogy of their compounds ; namely, the alliaceous odour of their vapour. Indeed, so great is the analogy between arsenic and phosphorus, that some chemists place arsenic among the metalloids. But it is a true metal, being a conductor of electricity, and having the metallic lustre. Still, the resemblance between arsenic and phosphorus shows that the line between metals and metalloids, especially in their chemical relations, cannot be sharply drawn.

The salts of arsenic acid give with nitrate of silver a brick-red precipitate, of tribasic arseniate of silver ;  $\text{AsO}_5 \cdot 3\text{AgO}$  : and with hydrochloric acid and sulphuretted hydrogen, a pale yellow precipitate of sulphuret of arsenic,  $\text{AsS}_3$ .

No modifications of arsenic acid, analogous to bibasic and monobasic phosphoric acids, are yet known.

#### ARSENIC AND CHLORINE, &c.

Terchloride of Arsenic.  $\text{AsCl}_3 = 181.5$ .

Prepared by distilling 6 parts of bichloride of mercury with 1 part of metallic arsenic,  $3\text{HgCl}_2 + \text{As} = 3\text{HgCl} + \text{AsCl}_3$ . It

is a colourless, volatile, fuming liquid, which is resolved, by the action of water, into hydrochloric and arsenious acids.  $\text{AsCl}_3 + 3\text{HO} = \text{AsO}_3 + 3\text{HCl}$ .

The teriodide of arsenic forms brick-red volatile anhydrous flakes, soluble in water, and crystallising in red hydrated crystals. A terbromide also exists as a volatile crystalline solid, at temperatures below  $68^\circ$ . The terfluoride is a colourless fuming liquid, corroding glass, and decomposed by water.

#### ARSENIC AND HYDROGEN.

When an alloy of arsenic and potassium is made to act on water, there is formed a brown solid body, which is said to be a bihyduret of arsenic,  $\text{AsH}_2 = 77$ .

Arseniuretted Hydrogen.  $\text{AsH}_3 = 78$ .

When arsenic is melted with an equal weight of zinc, an alloy is formed, which, when acted on by strong hydrochloric acid, yields a gas which is colourless, has a strong garlic odour, burns with a blue flame, and is distinguished from all other gases by being totally absorbed, when pure, by a saturated solution of sulphate of copper. At  $-40^\circ$  it liquefies, and is not frozen by a cold of  $-166^\circ$ . This substance is arseniuretted hydrogen, or terhydride of arsenic,  $\text{AsH}_3$ , corresponding to ammonia and to phosphuretted hydrogen. It is frightfully poisonous when respired even in very small proportion along with common air, and the incautious experimenting with it has proved fatal to more than one chemist. It acts on many metallic solutions, forming insoluble arseniurets. When heated to redness it is decomposed, arsenic being deposited, and hydrogen, equal to one and a half time the bulk of the gas, being separated. The gas is formed when hydrogen is generated in a liquid containing arsenious acid dissolved, and mixes with the hydrogen; and when the mixture is heated red-hot in passing through a tube, or burned, a cold plate being held in the flame, arsenic is deposited. This is the principle on which Marsh's process for detecting arsenious acid is founded.

#### ARSENIC AND SULPHUR.

Bisulphuret of Arsenic.  $\text{AsS}_2 = 107$ .

Formed by melting 1 eq. of arsenic with 2 of sulphur, or arsenious acid with half its weight of sulphur. It is a red translucent solid, which may be sublimed in close vessels. It occurs in the mineral kingdom as realgar. White Indian fire



used for signals, is composed of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

b. Tersulphuret of Arsenic.  $\text{AsS}_3 = 123$ .

Prepared by melting together equal weights of arsenious acid and sulphur, or by passing a current of sulphuretted hydrogen through a solution of arsenious acid. It has an orange yellow colour, is fusible, and may be sublimed in close vessels. It is very soluble in caustic alkalies, yielding colourless solutions. It occurs in the mineral kingdom as auripigmentum, or orpiment, and is an ingredient in king's-yellow. It may be used for dyeing silk, woollens, or cottons yellow, by soaking them in a solution of orpiment in ammonia, and then suspending them in a warm chamber. The ammonia evaporates, and the orpiment remains firmly fixed in the cloth. This sulphuret is the form in which arsenic is best separated from mixed liquids in medico-legal investigations.

c. Persulphuret of Arsenic.  $\text{AsS}_5 = 155$ .

Formed by the action of sulphuretted hydrogen on arsenic acid, or on arseniates acidulated by acetic acid. It is of a paler yellow than orpiment, is soluble in alkalies, fusible, and in close vessels volatile without change. It forms sulphur salts with the sulphurets of the alkaline metals.

34. CHROMIUM.  $\text{Cr} = 26\cdot7$ .

Occurs in nature, in union with oxygen, as chromic acid in chromate of lead, and as oxide of chromium in chrome iron ore, from which latter all the compounds of chromium are obtained. The metal is very infusible, and has probably never been completely melted. It is obtained with difficulty in hard coherent masses of an iron-grey colour, by heating the oxide to the highest temperature of a wind furnace for some hours in a crucible lined with charcoal. In this state it is hardly at all acted on by the strongest acids, but is oxidised by fusion with nitre, yielding chromic acid.

CHROMIUM AND OXYGEN.

a. Protoxide of Chromium.  $\text{CrO} = 34\cdot7$ .

This oxide is only known as hydrate, and is obtained by adding potash to a solution of the protochloride, as a dark brown precipitate, which absorbs oxygen rapidly, and even decomposes water, being converted into an intermediate oxide,  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3 = \text{Cr}_3\text{O}_4$ , which has the colour of Spanish snuff. The protoxide is a base, and though its salts with the common

acids are unstable from its affinity for oxygen, yet some of its double salts can be crystallised, and are more permanent. These double salts show that the protoxide belongs to the same group as the oxides, of magnesium, zinc, iron, &c.; for the double sulphate of protoxide of chromium and potash,  $\text{CrO}, \text{SO}_3 + \text{KO}$ ,  $\text{SO}_3 + 6 \text{ aq.}$  is isomorphous with the corresponding salt of protoxide of iron. It forms crystals of a fine blue colour.

b. Sesquioxide of Chromium.  $\text{Cr}_2\text{O}_3 = 77.4$ .

This oxide may be obtained by heating to redness the bichromate of potash,  $\text{KO}, 2\text{CrO}_3$ ; when neutral chromate,  $\text{KO}, \text{CrO}_4$ , is formed, sesquioxide is produced,  $\text{Cr}_2\text{O}_3$ , and oxygen is disengaged,  $2(\text{KO}, 2\text{CrO}_3) = 2(\text{KO}, \text{CrO}_3) + \text{Cr}_2\text{O}_3 + \text{O}_3$ . The neutral chromate is dissolved out by water and the oxide is obtained as a crystalline green powder; or it may be prepared by heating a mixture of bichromate with carbonate of soda and sal-ammoniac to redness. The hydrate is obtained by heating solution of bichromate with hydrochloric acid and alcohol or sugar till the liquid becomes of a pure green, and adding ammonia, which precipitates the hydrate as a pale bluish-green bulky powder.

Sesquioxide of chromium is isomorphous with sesquioxide of iron and alumina, and has been obtained in crystals exactly resembling specular iron ore. It is a weak base, and may be substituted for alumina or peroxide of iron in their salts, without altering the form. All its salts are green or blue, and most of them are red by transmitted candle-light. Oxide of chromium appears to exist in its salts in two modifications, in one of which the solutions are pure green, in the other of a violet tint. The oxide may be used for painting a beautiful green on china, and for giving glass a green colour, or as a paint, being very permanent.

The salts of sesquioxide of chromium are green, but readily pass into the apparently allotropic violet form. The violet salts crystallise more easily than the green ones. When they are precipitated by alkalis, they yield a bluish green hydrate, which, if not heated, reproduces the violet salts with acids. But if the solution of these salts be heated to boiling, it passes into the green form, the salts of which yield with alkalis a greyish green hydrate,  $\text{Cr}_2\text{O}_3, 10 \text{ aq.}$  The hydrate from the violet salts dissolves in ammonia, but the other only does so after long digestion, being converted into the violet form. Both forms dissolve in excess of potash or soda, forming green solutions, from which on boiling, hydrate of the green salts is deposited; this form of the green hydrate is said to be  $\text{Cr}_2\text{O}_3, 9 \text{ aq.}$  When heated, the hydrate loses all its water below redness, and is

then less soluble in acids. If heated a little farther, it suddenly glows, shrinks in volume, and is now insoluble in acids, indicating a third modification.

Sesquioxide of chromium has, like other sesquioxides, a strong tendency to form double salts. Thus the sulphate, which exists in three forms, a crystalline violet form,  $\text{Cr}_2\text{O}_3, 3\text{SO}_3, 15 \text{ aq.}$ ; an uncrystallisable but soluble green form,  $\text{Cr}_2\text{O}_3, 3\text{SO}_3, 5 \text{ aq.}$ ; and an insoluble red crystalline form, which is anhydrous,  $\text{Cr}_2\text{O}_3, 3\text{SO}_3$ , forms, when in the first of these states, double salts with the sulphates of potash, soda, and ammonia. These are the chrome-alums, which form crystals, black by reflected, purple by transmitted light, of the same form as alum. The potash salt is  $\text{KO}, \text{SO}_3 + \text{Cr}_2\text{O}_3, 3\text{SO}_3 + 24 \text{ aq.}$  These salts form with cold water violet solutions, in which, especially when diluted, green is also visible; and so long as heat is avoided may be re-crystallised; but if boiled, the sesquioxide passes into the green form, the solution becomes entirely green, and the alum no longer crystallises from it. Apparently the violet form alone yields these alums. The sesquioxide also yields apparently in the violet form a beautiful double salt, with oxalic acid and potash, which is remarkable for its optical properties.

When a mixture of 30 parts of stannic acid, 10 of chalk, and 1 of chromate of potash is ignited, the mass powdered, and well washed with weak hydrochloric acid, it yields a residue which gives, on china, a beautiful rose colour.

c. Chromic Acid.  $\text{CrO}_3 = 50.7$ .

Prepared by adding 1 vol. of a cold saturated solution of bichromate of potash to  $1\frac{1}{2}$  vol. of pure oil of vitriol, and allowing the mixture to cool in a covered capsule, or in a flask, when it deposits beautiful deep-red needles of chromic acid. The liquid being drained off, these are laid on a porous brick to dry, covered with a bell-jar. They must be preserved in very tightly-stoppered bottles, as they are highly deliquescent. To remove adhering sulphuric acid, the crystals are dissolved in water, and a solution of bichromate of baryta added as long as it causes a precipitate. The filtered liquid is evaporated to a small bulk, and finally crystallised by evaporation in vacuo over sulphuric acid. The crystals thus obtained are pure.

Chromic acid is a strong acid, isomorphous with sulphuric, selenic, and manganic acids. Its salts are yellow, orange, or red, and distinguished by the beauty and permanence of their colours. The acid itself is a powerful oxidising agent, yielding half its oxygen readily to oxidisable bodies, and being reduced to sesquioxide:  $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + \text{O}_3$ . Thus it instantly sets fire

to alcohol when thrown into that fluid; and a mixture of bi-chromate of potash and sulphuric acid is much used as a means of oxidising organic products, and yielding new compounds. Chromic acid and oxide of chromium are both easily recognised, in solutions by their colour, and the acid especially by its ready convertibility into the oxide by deoxidising agents.

According to Barreswill there exists a perchromic acid,  $\text{Cr}_2\text{O}_7$ , corresponding to permanganic acid. It is formed by the action of peroxide of hydrogen on chromic acid, and has a fine deep-blue colour. It is almost immediately resolved, however, into chromic acid and oxygen.

#### CHROMIUM AND CHLORINE.

##### a. Protochloride of Chromium. $\text{CrCl} = 61.7$ .

This chloride is obtained by heating the sesquichloride in a current of dry hydrogen, avoiding all traces of oxygen. It is a white solid, which dissolves in water, forming a blue solution. Blue seems to be the colour of the proto-compounds of chromium, as green and violet are of the sesqui-compounds, and yellow, orange, and red of chromic acid and its salts. The solution of the protochloride rapidly absorbs oxygen.

##### b. Sesquichloride of Chromium. $\text{Cr}_2\text{Cl}_3 = 159.9$ .

Prepared by passing chlorine over a mixture of sesquioxide of chromium and charcoal heated to redness. It collects in the cold part of the tube as a crystalline peach-blossom-coloured sublimate, which is insoluble in water, but by long contact with it undergoes a change, and then slowly dissolves, forming a green solution, which probably contains hydrochloric acid and sesquioxide,  $\text{Cr}_2\text{Cl}_3 + 3\text{H}_2\text{O} = \text{Cr}_2\text{O}_3 + 3\text{HCl}$ . The scales of anhydrous sesquichloride are instantly converted into the soluble green form by the contact of a few drops of the solution of the protochloride. When hydrated sesquioxide is dissolved in hydrochloric acid, a green solution is obtained, which, on evaporation, gives green crystals, said to be  $\text{CrO}_2\text{Cl}_2 \cdot 2\text{HCl} \cdot 10 \text{ aq.}$

If the violet sulphate of chromium (sesquioxide) be precipitated by chloride of barium, a violet sesquichloride (?) is obtained in solution, which is said to have the same formula as the green crystals last named, namely,  $\text{CrO}_2\text{Cl}_2 \cdot 2\text{HCl} + 10 \text{ aq.}$  But it is singular that in the green salt nitrate of silver precipitates only  $\frac{2}{3}$  of the chlorine present, while in the violet salt it precipitates the whole. This would seem to indicate that the two salts cannot have the same rational formula.

c. Oxychloride of Chromium.  $\text{Cr} \left\{ \begin{array}{l} \text{O}_2 \\ \text{Cl} \end{array} \right.$ , or  $\text{CrCl}_3 + 2\text{CrO}_3$ .

SYN. *Chlorochromic Acid*.—This compound is formed when neutral chromate of potash, common salt, and oil of vitriol are heated together,  $(\text{KO}, \text{CrO}_4) + \text{NaCl} + 2\text{SO}_3 = (\text{KO}, \text{SO}_3) + (\text{NaO}, \text{SO}_3) + \text{CrO}_2\text{Cl}$ ; or  $3(\text{KO}, \text{CrO}_3) + 3\text{NaCl} + 6\text{SO}_3 = 3(\text{KO}, \text{SO}_3) + 3(\text{NaO}, \text{SO}_3) + \text{CrCl}_3 + 2\text{CrO}_3$ . It distils over as a deep-red fuming liquid, which decomposes water, producing hydrochloric and chromic acids. It sets fire to phosphorus and many other combustible bodies. When its vapour is passed through a red-hot tube it is resolved into oxygen, chlorine, and sesquioxide of chromium,  $2\text{CrO}_2\text{Cl} = \text{Cr}_2\text{O}_3 + \text{O} + \text{Cl}_2$ ; or  $2(\text{CrCl}_3) + 2\text{CrO}_3 = 3\text{Cr}_2\text{O}_3 + \text{O}_3 + \text{Cl}_6$ . The sesquioxide here forms hard black crystals, isomorphous with corundum. Its constitution is uncertain, as, according to the two formulæ above given, it may be viewed either as chromic acid, in which 1 eq. of oxygen is replaced by chlorine, or as a compound of 1 eq. of terchloride of chromium with 2 eqs. of chromic acid.

d. Terfluoride of Chromium.  $\text{CrF}_3 = 83.7$ .

When a mixture of chromate of lead, fluoride of calcium, and oil of vitriol, or, better, fuming sulphuric acid, is distilled in a silver retort, there is disengaged a red gas, which, in contact with the moisture of the air, produces hydrofluoric and chromic acids. The production of it is as follows:  $\text{PbO}, \text{CrO}_3 + 3\text{CaF} + 4(\text{HO}, \text{SO}_3) = \text{PbO}, \text{SO}_3 + 3(\text{CaO}, \text{SO}_3) + 4\text{HO} + \text{CrF}_3$ . When the vapour of the terfluoride is conducted into a moistened platinum crucible, the vessel is soon filled with a light bulky scarlet wool of chromic acid, while hydrofluoric acid is given off,  $\text{CrF}_3 + 3\text{HO} = \text{CrO}_3 + 3\text{HF}$ .

e. Nitride of Chromium.  $\text{Cr}_3\text{N}_2$ ?

When the anhydrous sesquichloride of chromium is heated in a current of dry ammonia, chloride of ammonium sublimes, while a purple light is evolved, and a chocolate brown powder is left, which is said to be the nitride of the metal. It takes fire when heated in oxygen, and burns with a beautiful red light, forming sesquioxide of chromium, while nitrogen gas and red nitrous vapours escape.

Sesquisulphide of Chromium.  $\text{Cr}_2\text{S}_3 = 104.4$ .

This compound is formed when the vapour of bisulphide of carbon is passed over sesquioxide of chromium heated to a strong red heat in a porcelain tube. It appears in the form of black shining scales like those of graphite.

35. VANADIUM.  $V = 68.6$ .

This very rare metal is found in small quantity in the slag of the iron furnaces where the iron ore of Taberg, in Sweden, is smelted, also in the lead mines of Scotland, as vanadate of lead, a mineral which likewise occurs in Mexico. It is obtained by the action of potassium on vanadic acid, aided by heat, as a brilliant metallic powder. By passing a current of dry ammonia over heated chloride of vanadium, it is procured in a coherent film. The metal is brittle, very infusible, and nearly silver-white. In its chemical relations it is somewhat analogous to chromium; and, like it, forms coloured compounds. It is not oxidised either by air or water, and the only acid that dissolves it is aqua regia.

a. Protoxide of Vanadium.  $VO = 76.6$ .

A black powder, which being heated burns into deutoxide.

b. Deutoxide of Vanadium.  $VO_2 = 84.6$ .

This oxide, when anhydrous, is black, but forms blue salts these are apt to become first green and then red, from the formation of vanadic acid.

c. Vanadic Acid.  $VO_3 = 92.6$ .

Is obtained from vanadate of lead by dissolving it in nitric acid, and precipitating lead and arsenic by sulphuretted hydrogen, which reduces the acid to deutoxide. The blue solution is evaporated, during which vanadic acid is reproduced, and the dry mass is digested in ammonia, which dissolves the acid. Into this solution a lump of sal-ammoniac is introduced, and, as this dissolves, the vanadate of ammonia separates, being insoluble in a saturated solution of sal-ammoniac. When this salt is heated to a point below red heat in an open vessel, the ammonia is expelled, and vanadic acid left, which melts below redness, and on cooling forms beautiful red crystals. With bases it forms salts which are either red or yellow, according as they are acid or neutral salts. It is singular that the neutral vanadiates of the alkalies may occur both yellow and colourless without any known difference in composition. Vanadic acid unites with deutoxide of vanadium, forming compounds which are purple, green, yellow, or orange, according as the acid or oxide predominates. Vanadic acid is distinguished from chromic acid by yielding a blue solution, when deoxidised, instead of a green one. It also forms soluble and crystallisable compounds with various acids.

With chlorine, vanadium forms a bichloride,  $\text{VCl}_2$ , which is blue, and a terchloride,  $\text{VCl}_3$ . The latter is formed by passing chlorine over a mixture of protoxide of vanadium and charcoal, heated to low redness, when the terchloride distils over as a yellow fuming liquid, which decomposes water, producing hydrochloric and vanadic acids. When this chloride is exposed to a current of ammonia, a white compound is formed, and if this be heated in a continued current of ammonia, metallic vanadium is formed, and adheres to the tube. Bromide, iodide, and fluorides of vanadium have also been formed. The sulphides of the alkalis produce a brownish black precipitate in the salts of the binoxide, which dissolves in excess of the precipitants, forming a splendid purple solution. The salts of the binoxide and vanadic acid and its compounds, give, with tincture of galls, a deep black, of a remarkably intense colouring power. This would be the best ink known, as strong acids only turn it blue, while it is not changed by alkalis or by chlorine.

### 36. MOLYBDENUM. $\text{Mo} = 46$ .

This metal occurs in nature, combined with sulphur, forming a lead-coloured metallic mineral in broad plates or leaves, called molybdena, or sulphuret of molybdenum. It is found more sparingly as molybdic acid combined with lead. The metal may be obtained by passing hydrogen gas over molybdic acid, heated to whiteness in a porcelain tube. It is a brittle white metal, almost quite infusible. It forms three oxides.

### MOLYBDENUM AND OXYGEN.

#### a. Protoxide of Molybdenum. $\text{MO} = 54$ .

A black powder, which, when heated in the air, takes fire, and forms deutoxide. Its hydrate dissolves in acids.

#### b. Deutoxide of Molybdenum. $\text{MoO}_2 = 62$ .

This oxide is formed by heating a mixture of molybdate of soda with half its weight of sal-ammoniac. The residue, after any molybdic acid has been removed by digestion in potash, is the deutoxide, which is brown, but becomes purple when exposed to light. When molybdic acid is digested in hydrochloric acid along with copper filings, the liquid, if mixed with excess of ammonia, yields a rusty brown hydrate of the deutoxide. This hydrate dissolves in water, but is separated by the addition of saline matter. It forms with acids, reddish-brown salts, which, when anhydrous, are black.

If a solution of bichloride of molybdenum be added, drop by

drop, to one of molybdate of ammonia, the latter being concentrated, a deep blue precipitate is formed, which is a quadrimolybdate of the deutoxide;  $\text{MoO}_2 + 4\text{MoO}_3$ . This compound is also soluble in pure water, but is precipitated by any saline substance. When a small portion of the solution of a proto-salt of tin is added to the solution of any molybdate, this fine blue is produced, and thus serves as a test for the presence of molybdic acid. The bimolybdate of the deutoxide,  $\text{MoO}_2 + 2\text{MoO}_3$ , is green.

c. Molybdic Acid.  $\text{MoO}_3 = 70$ .

Obtained by roasting the sulphuret at a low red-heat as long as sulphurous acid escapes, and acting on the residue with ammonia, which dissolves molybdic acid. The molybdate of ammonia is then purified by crystallisation: and on heating it gently in an open platinum crucible, ammonia is expelled, and molybdic acid left. It is a white powder, fusible at a red-heat, which sublimes in a current of air. It is sparingly soluble in water. It forms salts with bases, which are colourless. It also dissolves in excess of acids when they are added to solutions of its salts, and in acid tartrate of potash. It has a tendency to form acid salts, some with 2 eq., some with 3, 4, or 5 eqs. of acid to 1 of base. The neutral molybdate of ammonia, and the acid molybdate, which is  $\text{NH}_4\text{O}$ ,  $2\text{MoO}_3$ , both crystallise readily.

Molybdate of ammonia is used as a test for small quantities of phosphoric acid. The substance to be tested must be dissolved, and the solution acidulated with hydrochloric acid. The molybdate being added, produces a yellow colour, and in a short time small yellow crystals are deposited, which are insoluble, which contain phosphoric acid, molybdic acid, and ammonia. The formation of this yellow salt may also be used to detect minute portions of ammonia. A quantity of the yellow salt is first prepared, then ignited to expel ammonia, digested with nitric acid to reoxidise any molybdic acid that may have lost oxygen; the nitric acid is expelled by heat, and the residue is dissolved in carbonate of soda, and hydrochloric acid added in excess. This solution will easily detect, it is said, 1 part of sal-ammoniac in 10,000 of water. It has no action on salts of soda, but in strong solutions of salts of potash it forms a similar yellow salt.

MOLYBDENUM AND CHLORINE.

The protochloride,  $\text{MoCl}$ , is a nearly black soluble compound. When chlorine gas is passed over metallic molybdenum gently heated, bichloride of molybdenum,  $\text{MoCl}_2$ , is



formed as a deep-red vapour, which condenses in black crystals like iodine. When the deutoxide is heated in dry chlorine, there is formed a yellowish-white crystalline sublimate, which is an oxychloride, analogous to that of chromium,



## MOLYBDENUM AND SULPHUR.

There are 3 sulphurets of this metal. 1. The bisulphuret,  $\text{MoS}_2$ , which is the usual ore of molybdenum already described; 2. The tersulphuret, a dark-brown or black powder,  $\text{MoS}_3$ ; 3. The persulphuret, also a dark powder,  $\text{MoS}_4$ . Both the last are sulphur acids, combining with sulphur bases, such as sulphuret of potassium. The compound of tersulphide of molybdenum with sulphuret of potassium,  $\text{KS, MoS}_3$ , is a most beautiful salt, having a metallic lustre like that of the golden beetle.

37. TUNGSTEN.  $\text{W} = 95$ .

SYN. *Wolfram*.—Occurs in nature, chiefly in the mineral wolfram, oxidised, along with oxides of iron and manganese, and more sparingly in the mineral tungsten, a compound of tungstic acid with lime. The metal may be obtained as the preceding, but is little known. It is very infusible, and has the Sp. G. 17.4. When heated in air, it burns and forms tungstic acid.

## TUNGSTEN AND OXYGEN.

a. Deutoxide of Tungsten.  $\text{WO}_2 = 111$ .

To obtain it, 1 part of finely-powdered wolfram is fused in a platinum crucible with 2 parts of carbonate of potash. Tungstate of potash is formed, which is dissolved, filtered to separate the oxides of iron and manganese, and evaporated to dryness. The salt is mixed, in solution, with half its weight of sal-ammoniac, and the mixture dried up and ignited. The tungstic acid is reduced to the state of oxide by the ammonia, and chloride of potassium is formed; the latter is dissolved out by water, and the former, being first boiled with potash to remove any tungstic acid, and then washed and dried, is pure oxide of tungsten. It is a very heavy black powder, which, when heated in the air, burns like tinder, forming tungstic acid. When the bitungstate of soda is heated in hydrogen, there is left a compound in gold-coloured cubes, with metallic lustre, which is composed of soda and the deutoxide,  $\text{NaO} + 2\text{WO}_2$ . It is insoluble in all menstrua except hydrofluoric acid.

b. Tungstic Acid.  $\text{WO}_3 = 119$ .

It is formed, as above, by heating the oxide in the air. It is a yellow powder, insoluble in water. With bases, it forms crystallisable salts. When heated to  $500^\circ$  or  $600^\circ$  in a current of hydrogen, it becomes of a fine deep-blue, losing so much oxygen that it leaves an oxide, the blue oxide of tungsten, the formula of which is  $\text{W}_2\text{O}_5 = \text{WO}_2 + \text{WO}_3$ ; so that it may be viewed as a tungstate of tungsten.

## TUNGSTEN AND CHLORINE.

When heated in chlorine gas, tungsten forms two chlorides, a bichloride,  $\text{WCl}_2$ , and a terchloride,  $\text{WCl}_3$ . Both are red, volatile, and crystallisable compounds, subliming in beautiful crystals. The former, with water, produces hydrochloric acid and binoxide of tungsten; the latter yields hydrochloric acid and tungstic acid. The bichloride absorbs ammonia, and when this compound is heated, sal-ammoniac is expelled, and a compound of nitride and amidide of tungsten is left as a black powder,  $2\text{WN} + \text{WNH}_2$ .

When the binoxide is heated in chlorine gas, there is formed an oxychloride in the shape of white volatile scales, like boracic acid. It is  $\text{WCl}_3 + 2\text{WO}_3$ ; or  $\text{W} \begin{cases} \text{O}_2 \\ \text{Cl} \end{cases}$ .

The sulphurets of tungsten have no peculiar interest.

38. COLUMBIUM.  $\text{Ta} = 92$ .

**SYN. *Tantalum*.**—It occurs very sparingly in the minerals tantalite and yttrio-tantalite, as columbic acid. The metal is obtained by the action of potassium on the double fluoride of columbium and potassium, as a black powder, which, when compressed, exhibits metallic lustre; and when heated burns in air, yielding columbic acid.

With oxygen it appears to form two compounds; an oxide and columbic acid. The latter is a white insoluble powder, which forms salts with bases.

With chlorine it forms a volatile chloride,  $\text{TaCl}_3$ ; and with fluorine, a white soluble fluoride,  $\text{TaF}_3$ . The formulæ of these compounds are not quite fixed. According to the equivalent above given, the acid should be a sesquioxide; by the old or double equivalent it was a teroxide. The same remark applies to the chloride and fluoride.

Rose has announced the existence of two new metals found in the ores of columbium or tantalum, to which he has given the

names of pelopium and niobium : and Herrman states that the Siberian ytthro-tantalite contains another new metal, ilmenium. Columbium seems to have considerable analogies with silicon.

### 39. ANTIMONY. $\text{Sb} = 120\cdot3$ .

This valuable metal is chiefly found in the mineral called antimony, which is a tersulphuret,  $\text{SbS}_3$ , and which occurs both pure and combined with other sulphurets. From the sulphuret the metal is easily obtained by heating it with iron filings, when the sulphur combines with the iron, and the melted antimony collects at the bottom of the crucible. Or 4 parts of the sulphuret is mixed with 3 of tartar, and  $1\frac{1}{2}$  of nitre, and the mixture thrown, in small portions, into a crucible kept at a full red-heat. The sulphur is oxidised by the nitre, and a button of metal is found at the bottom of the crucible.

But the metal is apt to retain portions of arsenic and other metals. It is purified by heating it with nitrate and carbonate of soda, when the whole is oxidised ; but water afterwards dissolves arseniate of soda, leaving the antimoniate undissolved, and from this salt the antimony is reduced by heating with tartar. It now contains potassium. It is broken into small pieces and placed in water, when the potassium dissolves, and the metal falls to powder. One third of this is oxidised by nitric acid, and heated with the rest, when a regulus of pure antimony is obtained, any lead or iron that may be present being dissolved by the oxide, which melts and forms a flux.

On the large scale, the ore is roasted, and thus converted into a mixture of oxide and sulphide ; this is mixed with charcoal, and made into a paste with a strong solution of carbonate of soda, and heated to full redness, when the metal collects in the bottom of the crucible.

It is a brittle metal, of Sp. Gr.  $6\cdot7$ , having a bluish or greyish-white colour when pure. It melts at  $810^\circ$ , and in a very intense heat it is volatilised. When heated strongly in open vessels, it takes fire, burning with a white light, and producing white vapours, which often condense in crystals, and are teroxide of antimony,  $\text{SbO}_3$ . Antimony is the chief ingredient in type metal.

### ANTIMONY AND OXYGEN.

#### a. Teroxide of Antimony. $\text{SbO}_3$ $144\cdot3$ .

To prepare it, tersulphuret of antimony is boiled with about 5 parts of strong hydrochloric acid, when sulphuretted hydrogen is given off, and terchloride of antimony is dissolved.  $\text{SbS}_3 + 3\text{HCl} = \text{SbCl}_3 + 3\text{HS}$ . The solution is now thrown into a large

quantity of water, when a curdy precipitate separates, which is teroxide of antimony, combined with some undecomposed chloride,  $9\text{SbO}_3 + 2\text{SbCl}_3$ , the oxide having been formed by the action of water on the chloride;  $\text{SbCl}_3 + 3\text{HO} = \text{SbO}_3 + 3\text{HCl}$ . The precipitate of oxychloride, which soon changes into crystals, if left in the liquid, is now to be washed and digested with an excess of carbonate of soda, by which the remaining chloride is converted into oxide.  $\text{SbCl}_3 + 3(\text{NaO}, \text{CO}_2) = \text{SbO}_3 + 3\text{NaCl} + 3\text{CO}_2$ . The teroxide is now pure, and is to be washed and dried. Or metallic antimony is boiled to dryness with oil of vitriol in an iron vessel, and the subsulphate left is decomposed by carbonate of soda, when it yields the oxide.

It is a greyish-white heavy powder, fusible at a dull red-heat in close vessels, and volatile at a higher temperature. If heated in the open air it absorbs oxygen, forming antimonious acid. It is a base, and forms salts with acids, the most important of which is tartar emetic. Most of its soluble salts are decomposed by the contact of water, but the precipitate is instantly dissolved on the addition of tartaric acid.

Teroxide of antimony in solution is easily recognised by the peculiar brownish orange precipitate caused by sulphuretted hydrogen.

b. Antimonious Acid.  $\text{SbO}_3 = 152\cdot3$ .

When teroxide of antimony is heated, it absorbs oxygen, and when antimonious acid is heated, it loses oxygen, the product in both cases being the permanent oxide, called antimonious acid. It is a white insoluble powder, very infusible and fixed in the fire. It seems, however, to be rather a compound of antimonious acid with the teroxide,  $\text{SbO}_3 + \text{SbO}_3 = 2(\text{SbO}_4)$ .

c. Antimonic Acid.  $\text{SbO}_5 = 160\cdot3$ .

Is formed by acting on the metal with strong nitric acid till it is converted into a white powder, which is hydrated antimonic acid. By a moderate heat it is rendered anhydrous, when it has a pale yellow colour. It appears to form two modifications, one monobasic, the other bibasic. The latter is called metantimonic acid. It is decomposed by a red-heat, yielding water, oxygen, and antimonious acid. It forms salts, called antimoniates, with bases. That of soda being insoluble, antimoni-ate of potash which is soluble, is used as a test for soda.

All the oxides of antimony are used in medicine; but the teroxide is the most important, as the basis of tartar emetic, which is a double tartrate of potash and teroxide of antimony.

Antimony seems to form a gaseous compound with hydrogen,

analogous to arseniuretted hydrogen, which is not yet known in a state of purity. It takes fire when heated in air, and in burning forms oxide, and deposits on cold substances held in the flame crusts of the metal, somewhat like those of arsenic. The means of distinguishing them are mentioned under arsenic.

## ANTIMONY AND CHLORINE.

a. Terchloride of Antimony.  $\text{SbCl}_3 = 226.8$ .

Is readily obtained by dissolving 1 part of sulphuret of antimony in 5 parts of hydrochloric acid (see above), and distilling the solution, until the volatile part becomes semi-solid on cooling; the receiver is then changed, and what passes over afterwards is pure anhydrous terchloride of antimony. It is a soft deliquescent solid, formerly called butter of antimony. When mixed with water, it is decomposed as mentioned above.

b. Perchloride of Antimony.  $\text{SbCl}_5 = 297.8$ .

Obtained by acting on metallic antimony, or on the terchloride, with an excess of chlorine. It is also formed when powdered antimony is introduced into chlorine gas, when it burns with a vivid light. It is a colourless, volatile fuming liquid, which is decomposed by water, yielding hydrochloric and antimonious acids.

c. Oxychloride of Antimony.  $9\text{SbO}_3 + 2\text{SbCl}_3$ .

This is the white powder formed when terchloride of antimony is thrown into water, as above described, under the head of teroxide. It soon changes into crystals, and is a definite compound of oxide and chloride. It is entirely converted into oxide by alkalis. It was formerly called powder of Algaroth.

Bromine and antimony combine readily, and form a volatile crystalline solid.

## ANTIMONY AND SULPHUR.

a. Tersulphuret of Antimony.  $\text{SbS}_3 = 168.3$ .

This is the common ore of antimony, and is generally a dark-gray radiated fusible crystalline mass, Sp. G. 4.62. When formed by the action of sulphuretted hydrogen on salts of antimony, it is precipitated as a hydrate of a brownish orange colour. When the tersulphide is boiled with alkalis, it dissolves, and on cooling deposits an orange powder, called kermes mineral. This is a mixture of tersulphide and teroxide.

b. Persulphuret of Antimony.  $\text{SbS}_5 = 209$ .

When tersulphuret and sulphur are boiled in solution of

potash, and an acid added to the filtered liquid, a golden-yellow precipitate is formed, often called the golden sulphuret of antimony, which is the persulphuret,  $\text{SbS}_5$ . It may also be formed by passing sulphuretted hydrogen through an acid solution of the perchloride. It is a sulphur acid, and combines readily with the sulphurets of the alkaline metals. The compound with sulphuret of sodium forms large crystals.

c. Oxysulphuret of Antimony.  $2\text{SbS}_3 + \text{SbO}_3$ .

This compound is found in nature as red antimony : and when tersulphuret of antimony is boiled with potash, and the liquid allowed to cool, a reddish orange precipitate is formed, which is often oxysulphuret ; although it may be obtained nearly free from oxide, and is then hydrated tersulphuret. This is the substance so long known as mineral kermes ; and it is the form in which sulphuret of antimony is chiefly used in medicine on the Continent. In this country we use the precipitated tersulphuret.

40. URANIUM.  $\text{U} = 217.2?$  or 60?

This metal occurs in the form of black oxide, along with other oxides in the mineral pitchblende ; and in that of sesquioxide in uranite and uran mica. When an excess of pitchblende is digested with diluted nitric acid, uranium dissolves, to the exclusion of iron, and after lead, copper, bismuth, or arsenic, have been removed by sulphuretted hydrogen, the solution may be considered pure. On evaporation it yields beautiful crystals of the nitrate of the sesquioxide, which have a fine yellow colour with green reflexions. Heated to redness, it leaves an oxide, which is mixed with charcoal, heated to redness, and chlorine passed over it. By this means a green volatile protochloride sublimes, which, when heated with potassium, yields the metal.

Uranium is white and slightly malleable ; permanent in air and water at ordinary temperatures, but burning brightly when heated in air. It dissolves in hydrochloric and sulphuric acid, hydrogen being liberated. It is more analogous to iron and manganese, in its chemical relations, than to any other metals.

URANIUM AND OXYGEN.

The protoxide is obtained anhydrous by heating the protoxalate to redness in close vessels. It forms, with acids, green crystallisable salts, but the anhydrous oxide does not dissolve in acids, though its hydrate does. Its formula is said to be  $\text{UO}$ , adopting the new equivalent 60 for the metal.

The black oxide,  $2\text{UO} + \text{U}_2\text{O}_3 = \text{U}_4\text{O}$ , is obtained by strongly igniting the protoxide in air, or by calcining the nitrate of the sesquioxide. It is a dense powder of a pure and intense black colour, much used in painting on china.

The green oxide,  $\text{UO} + \text{U}_2\text{O}_3 = \text{U}_3\text{O}_4$ , is produced by gently igniting the protoxide in air or oxygen; it dissolves in hot sulphuric acid, but does not form distinct salts.

These two oxides, the black and the green, correspond exactly to the two magnetic oxides of iron; and the green oxide corresponds also to the red oxide of manganese.

The sesquioxide,  $\text{U}_2\text{O}_3$ , corresponding to the sesquioxides of iron and manganese, is not easily obtained pure, having a strong tendency to combine with the bases used to separate it from its salts. It is said that a hydrate of it,  $\text{U}_2\text{O}_3, 2 \text{ aq.}$  may be obtained by exposing a solution of the oxalate of the sesquioxide to the sun's rays, when a brownish-violet hydrate of the green oxide is deposited. This absorbs oxygen from the air, and is converted into a greenish-yellow hydrate of the sesquioxide. When heated to not more than  $572^\circ$ , it leaves the anhydrous peroxide as a brick-red powder. Its salts have a fine canary-yellow colour, often mixed with reflexions of pale green. The alkalies decompose them, but the yellow precipitate is not sesquioxide, but a uranate of the alkali employed. The yellow sesquioxide, or peroxide of commerce, is a hydrated uranate of ammonia, which, when heated, leaves the black or green oxide, or a mixture of both. The uranates of the earths are not decomposed by a red heat, and are much used in giving to glass the beautiful yellow and green colour so much admired in Bohemian glass.

#### URANIUM AND CHLORINE.

The protochloride,  $\text{UCl}$ , prepared as above described, is green, volatile, deliquescent, and is decomposed by water. Heated to redness in a current of hydrogen, it is converted into a subchloride,  $\text{U}_4\text{Cl}_3$ , which forms slender dark-brown acicular crystals, very soluble in water, forming a deep purple solution. From this solution, ammonia precipitates a brown suboxide, which rapidly absorbs oxygen from the air.

When chlorine is passed over the protoxide, an oxychloride,  $\text{U}_2\text{ClO}_2$ , or  $(2\text{U}_2\text{O}_3 + \text{U}_2\text{Cl}_3)$  is formed. It is deliquescent, forms a yellow solution with water, and yields with the alkaline chlorides, double salts which crystallise. That with chloride of potassium is  $\text{KCl}, \text{U}_2\text{ClO}_2$ , or  $3\text{KCl} + (2\text{U}_2\text{O}_3 + \text{U}_2\text{Cl}_3)$ . It forms rhombic tabular prisms of a greenish-yellow colour.

The other compounds of uranium are little known. Sulphide of ammonium produces with the salts of the protoxide a black protosulphide, and with those of the sesquioxide a yellowish-brown sesquisulphide. Ferrocyanide of potassium gives, with the salts of the sesquioxide, a rich chesnut-brown precipitate, and infusion of galls a dark brown.

There is still some doubt as to the equivalent of uranium; the number given in the table of equivalents, 217, was that long adopted, up to the period of Peligot's researches. The formulæ above given refer to the smaller number 60, which, for the present, is the more probable.

41. CERIUM. Ce = 47. 42. LANTHANUM. La = 47?

These metals are in a state of still greater uncertainty. They occur invariably associated in some very rare minerals, of which, cerite, a hydrated subsilicate, is the most important, and are not yet known in a state of purity. This applies to the oxides likewise. According to the most recent researches of Mosander, who discovered lanthanum, these two metals appear to be always associated with a third, didymium, which is not yet fully described.

Cerium forms two oxides, a protoxide and a sesquioxide, both of which form salts with acids. The double sulphate of protoxide of cerium and potash is insoluble in sulphate of potash. The oxalate of the protoxide is a white insoluble powder. The sesquioxide is yellowish, and its salts are yellow or red.

Lanthanum forms only one oxide, which is buff coloured and very soluble in dilute nitric acid. Its salts are colourless and astringent, and give a white precipitate with soluble oxalates.

Didymium forms also but one oxide, which, in the anhydrous state, is dark brown. Its salts have a pink or amethyst colour and sulphide of ammonium does not precipitate their colour solutions.

43. BISMUTH. Bi = 71, or 213.

Occurs frequently as metal, sometimes as sulphuret. The commercial bismuth is never quite pure, containing a little sulphur and arsenic, besides silver, lead, and iron. The two former are removed by melting the metal with  $\frac{1}{10}$ th of nitre. It is then dissolved in nitric acid, and the solution poured into a large mass of water. A sparingly soluble subnitrate is formed, which is washed, dried, and reduced by fusion with  $\frac{1}{10}$ th of charcoal. It is a highly crystalline metal, of a reddish-white colour, fusible at  $476^{\circ}$ , and even volatile in close vessels. When



heated in the air it burns with a bluish flame, forming oxide of bismuth. Bismuth is an ingredient in Newton's fusible metal, and in various fusible alloys.

## BISMUTH AND OXYGEN.

a. Protoxide or teroxide of Bismuth.  $\text{BiO} = 79$ , or  $\text{BiO}_3 = 237$ .

To obtain it, bismuth is dissolved in nitric acid, and the solution thrown into water, when a copious white precipitate of subnitrate of bismuth is formed. This is washed, dried, and ignited, and protoxide of bismuth is left. It is a yellow powder, fusible at a red-heat. A hydrate of this oxide is formed when an excess of ammonia acts on the salts of bismuth. With acids it forms colourless salts. Most of these salts are decomposed when thrown into water; and this character, coupled with the black precipitate caused by sulphuretted hydrogen, enables us easily to recognise the presence of bismuth, and to separate it from other metals.

b. Peroxide of Bismuth, or Bismuthic Acid.  $\text{BiO}_5 = 253$ ?

It is obtained by passing chlorine through the hydrated teroxide, suspended in strong solution of potash, when a blood-red solution of bismuthate of potash is obtained, with a red precipitate, which is to be well washed, and digested in cold nitric acid to remove the oxide always mixed with it. It is then hydrated bismuthic acid,  $\text{HO, BiO}_5$ . At  $270^\circ$  it becomes brown and anhydrous. More strongly heated it loses oxygen, forming an intermediate oxide, or bismuthate of bismuth, probably  $\text{BiO}_3 + \text{BiO}_5 = 2\text{BiO}_4$ . The alkaline bismuthates are decomposed by water.

The equivalent of bismuth has long been doubtful, as well as the composition of its oxides. Recent researches, however, tend to show that the higher number, 213, is the more probable; and that the two oxides correspond to those of antimony and arsenic, and are, therefore, a teroxide and an acid, with 5 eqs. of oxygen to 1 of metal.

Terchloride of Bismuth.  $\text{BiCl}_3 = 319.5$ .

Powdered bismuth takes fire in chlorine gas, and forms a grey semi-solid chloride, not volatile, the old butter of bismuth. It is decomposed by excess of water, forming an oxychloride,  $\text{BiCl}_3 + 2\text{BiO}_3$ , known as pearl white.

Bromide of bismuth resembles iodine in appearance; it is fusible and volatile. The iodide is dark brown.

The sulphuret of bismuth found in nature is of a lead-grey.

colour, and isomorphous with tersulphide of antimony; that formed by the action of sulphuretted hydrogen on the salts of bismuth is black. It is a protosulphuret,  $\text{BiS}$ .

#### 44. TITANIUM. $\text{Ti} = 25$ .

This metal is found oxidised in several minerals; and occurs occasionally in the form of a remarkable compound, in the slag of iron-works, as small cubical crystals, exactly similar to copper in appearance, of Sp. G. 5.3, and very infusible. When heated with nitre, they are oxidised, producing titanic acid. These crystals were long regarded as metallic titanium, but Wöhler showed that they contain 18 per cent. of nitrogen, and are a compound of nitride and cyanide of the metal,  $\text{TiCy} + 3\text{Ti}_3\text{N}$ . In Canada, rocky beds occur in which titaniferous iron ore, and probably other compounds of titanium are abundantly disseminated. The metal is obtained by the action of potassium on the titanofluoride of potassium, as a grey amorphous powder, which burns with great brilliancy when heated in oxygen.

#### TITANIUM AND OXYGEN.

##### a. Protoxide of Titanium. $\text{TiO}$ ?

The protoxide is said to be formed when titanic acid is heated in a crucible lined with charcoal, as a black powder, insoluble in acids, which is oxidised by fusion with nitre.

When a solution of titanic acid in hydrochloric acid is acted on by zinc, a purple powder is thrown down, which is supposed to be a hydrate of the sesquioxide. It rapidly absorbs oxygen from the air, and is reconverted into titanic acid.

##### b. Titanic Acid. $\text{TiO}_2 = 41$ .

To obtain this acid, rutile, which is a native titanate of iron and manganese, is heated to strong redness in a porcelain tube and sulphuretted hydrogen gas passed over it, which acts on the oxides of iron and manganese, converting them into sulphurets; the operation is continued as long as water is formed and the residue is digested in hydrochloric acid, which dissolves the sulphurets, leaving the titanic acid, mixed with a little sulphur. Should it not appear quite white, the process is repeated. Or rutile in fine powder is fused with carbonate of potash, and the residue treated with hot water, which leaves impure titanate of potash. This is dissolved in hydrochloric acid, precipitated by excess of ammonia, and the whole digested with sulphide of ammonium, which converts the other metals into sulphides

Sulphurous acid now dissolves these sulphides, and white titanitic acid is left.

Titanic acid is a snow-white infusible solid, in its relations somewhat analogous to stannic acid. It exists, like that acid, in two isomeric or allotropic forms, which indeed occur in nature. There are even three crystallised varieties found: rutile, of Sp. G. 4.25; brookite, of Sp. G. 4.03; and anatase, of Sp. G. 3.9; all in different forms. When titanitic acid, though pure and white, is strongly ignited, it becomes yellow or brown, and insoluble in acids, except hydrofluoric acid. When it has been fused with alkali, it becomes soluble in strong hydrochloric acid, but it is precipitated by boiling. Carbonate of ammonia, added to the acid solution, gives a precipitate of hydrated titanitic acid, which is white and gelatinous, and dissolves in diluted hydrochloric acid. A solution of galls causes an orange-red precipitate in its solution, and a rod of zinc causes a purple deposit. Titanitic acid is used in making the finer kinds of enamel for artificial teeth, from its whiteness and hardness.

#### BICHLORIDE OF TITANIUM.

Formed by passing chlorine gas over metallic titanium, or a mixture of titanitic acid and charcoal, at a red-heat. It is a transparent colourless liquid, boiling at a little above  $212^{\circ}$ , and fuming strongly in the air. When a few drops of water are added to a portion of it, a very violent action takes place, and a solid hydrate of titanitic acid is left, hydrochloric acid being given off.  $\text{TiCl}_2 + 2\text{H}_2\text{O} = \text{TiO}_2 + 2\text{HCl}$ . It absorbs a large quantity of ammonia, and yields a solid compound.

Bisulphuret of titanium is formed by passing the vapour of bisulphuret of carbon over titanitic acid, at a white heat.  $\text{CS}_2 + \text{TiO}_2 = \text{CO}_2 + \text{TiS}_2$ . It forms thick, green masses, which become yellow and metallic-looking by friction.

#### NITRIDES OF TITANIUM.

It has been already mentioned that the red metallic-looking crystals found in the slag of iron furnaces, and formerly supposed to be metallic titanium, really contain a nitride of the metal,  $\text{Ti}_3\text{N}$ , united with the cyanide. This nitride is unknown in the pure state. There is another nitride,  $\text{Ti}_3\text{N}_2$ , which is obtained when ammonia-chloride of titanium is ignited in a current of ammonia. It appears in the form of copper-coloured scales, which were at first supposed, like the iron-slag crystals, to be metallic titanium.

45. TELLURIUM.  $\text{Te} = 64.2$ .

This very rare metal occurs alloyed with gold, silver, bismuth, copper, and lead. The most frequent ore is the foliated black tellurium of Nagyag, in which it is combined with gold, silver, and lead, mixed with the sulphides of lead and antimony. It is purified by tedious processes, and with difficulty. It has a colour between that of tin and lead, is very brittle, and has the Sp. G. 6.2578. It is very fusible, and volatile at a red-heat. It forms two oxides. The first, oxide of tellurium or tellurous acid,  $\text{TeO}_2$ , is analogous to selenious acid, and like it formed by the action of nitric acid on the metal. It is a white insoluble powder, which forms with the alkalis crystallisable salts, from which it is separated by acids as a flaky hydrate, which dissolves in acids, and even in water. It is blackened by sulphuretted hydrogen, and reduced to the metallic state by zinc and other metals. The other oxide is telluric acid,  $\text{TeO}_3$ , which is formed when tellurium is deflagrated with nitre. It is a soluble and crystallisable acid; the crystals are  $\text{TeO}_3, 3\text{HO}$ . Its salts are not much known.

There are two chlorides: the protochloride,  $\text{TeCl}$ , a black solid, yielding a violent vapour; and the bichloride, a white volatile, crystallisable solid.

With sulphur, tellurium forms two compounds, one of which the bisulphuret,  $\text{TeS}_2$ , is a dark-brown powder; the other is yellow, but not permanent.

With hydrogen, tellurium forms a gaseous compound, obtained by the action of hydrochloric acid on an alloy of tellurium with zinc. It is a feeble acid, analogous in composition, smell, and other characters, to sulphuretted hydrogen. With water it forms a claret-coloured solution, which precipitates many metallic salts, yielding precipitates which are tellurets of the metals, analogous to the sulphurets and seleniurets. Its formula is  $\text{HTe}$ , and its action on metallic oxides is  $\text{HTe} + \text{MO} = \text{MTe} + \text{HO}$ . Dr. Simpson has observed that compounds of tellurium, in very small doses, communicate to the breath, and indeed to the whole person, the most intolerable fetor, lasting for weeks and even months after one small dose. The person who takes it is unavoidably banished from all society. This would indicate some peculiar action on the system.

Though quite metallic in appearance, tellurium is, perhaps more allied to the metalloids, especially to sulphur and selenium. It is not nearly so good a conductor of heat and electricity as most of the metals are, and by many chemists it is classed with the metalloids. We have here another strongly marked group

of three analogous elements ; and in this group also. the equivalent of the middle member, selenium, is the mean between those of sulphur and tellurium. The same relation, as we have seen, is found in the groups of chlorine, bromine, and iodine, of lithium, sodium, and potassium, and of barium, strontium, and calcium, and very nearly in that of phosphorus, arsenic, and antimony. We also see in tellurium, another proof that the metals and metalloids cannot be always sharply distinguished.

#### 46. COPPER. $\text{Cu} = 31.7$ .

This important metal is sometimes found as metal, but it chiefly occurs in copper pyrites, the sulphuret of copper and iron ; in blue copper ore, and in malachite, which are carbonates of copper. The latter ore, heated with charcoal, yields the metal most easily. It is distinguished from all other metals by its red colour. It melts in a strong red-heat, and has the Sp. G. 8.921 to 8.952. It is both ductile and malleable, and has a high degree of tenacity. It is hard, elastic, and sonorous. Heated in the open fire it absorbs oxygen, and produces a black crust of oxide of copper,  $\text{CuO}$ . Finely divided copper, as when reduced by hydrogen, takes fire when touched with a burning body, and glows, forming oxide. In the oxyhydrogen flame, copper burns with a green flame, and copper gives a green colour to flame in general. It is dissolved by boiling oil of vitriol, but its proper solvent is nitric acid ; it dissolves in all acids if air be admitted, even in the cold. This renders its use for culinary purposes dangerous, as copper vessels left with vinegar, or any vegetable acid in them, are sure to be corroded, and the solutions are very poisonous. Copper is an ingredient of brass, in which it is combined with zinc ; and of bronze and bell-metal, in which it is alloyed with different proportions of tin.

#### COPPER AND OXYGEN.

a. Protoxide of Copper.  $\text{CuO} = 39.7$ .

**SYN.** *Black Oxide of Copper*—Is obtained, as above, by heating copper in air, or by calcining nitrate of copper, when the oxide is left. It is a heavy black powder, which is a strong base, and forms with acids, salts, all of which are blue or green. The solutions of this oxide have generally a blue colour ; they give with potash a pale-blue hydrate, becoming black and anhydrous when boiled in the liquid in which it was formed ; with ammonia in excess a deep violet-blue solution ; with sulphuretted hydrogen, a black ; and with ferrocyanide of potassium, a chestnut-

brown precipitate. The last test is highly delicate. Iron throws down metallic copper from these solutions. Black oxide of copper is not decomposed by heat, but has the valuable property of yielding all its oxygen at a red-heat to organic matter; hence its importance in organic analysis.

b. Suboxide of Copper.  $\text{Cu}_2\text{O} = 71.4$ .

SYN. *Red Oxide of Copper*—Occurs native, and is formed when a mixture of dried sulphate of copper, dried carbonate of soda and copper filings, is ignited strongly for 20 minutes, or by boiling diacetate of copper with sugar, when the suboxide is deposited in minute red octohedrons. By the first process, it is obtained as a red powder. It dissolves in hydrochloric acid, forming a colourless solution, from which alkalis precipitate an orange hydrate,  $4\text{Cu}_2\text{O} + \text{aq.}$ , but most acids resolve it into black oxide and copper.  $\text{Cu}_2\text{O} = \text{CuO} + \text{Cu}$ . It is a feeble base. Red oxide of copper is used in making stained glass, to which it gives a fine ruby or purple colour.

Hydride of copper,  $\text{Cu}_2\text{H}$ , is formed when hypophosphorous acid is added to sulphate of copper. It is a brown powder, resolved, suddenly, at  $140^\circ$  into copper and hydrogen.

#### COPPER AND CHLORINE.

Chloride of Copper.  $\text{CuCl} = 67.2$ .

Forms green deliquescent needles, which are a hydrate. The anhydrous chloride is yellow. It is best prepared by dissolving the black oxide in hydrochloric acid, and evaporating, when green crystals are deposited,  $\text{CuCl} + 2 \text{aq.}$ , which are rendered anhydrous by being heated in close vessels. It forms double salts with alkaline chlorides, containing 1 eq. of each chloride. It absorbs ammonia, and forms a blue powder,  $\text{CuCl}, 3\text{NH}_3$ . Heat converts this into a green compound,  $\text{CuCl}, \text{NH}_3$ , or  $\text{N}^{\text{H}}_{\text{Cu}} \} \text{Cl}$ . The latter formula represents the chloride of ammonium, in which 1 eq. of hydrogen has been replaced by copper; or, as it has been called, chloride of cuprammonium. By passing ammonia through a strong solution of chloride of copper till the precipitate at first formed is redissolved, the liquid, on cooling, deposits small dark-blue crystals, which are  $\text{CuCl}, 2\text{NH}_3 + \text{aq.}$

Dichloride of Copper.  $\text{Cu}_2\text{Cl} = 98.9$ .

Is found when copper filings are heated with 2 parts of corrosive sublimate. A resinous-like fusible mass, of a yellow

or brown colour. Its solution in hydrochloric acid, on exposure to air, deposits a bluish-green oxychloride, which is Brunswick green. The dichloride forms double salts with the alkaline chlorides.

Diniodide of Copper.  $\text{Cu}_2\text{I} = 190.5$ .

Formed when iodide of potassium is added to a solution of 1 part of sulphate of copper, and 3 parts of sulphate of iron. It falls as a dirty white precipitate. We are thus enabled to precipitate the whole of the iodine from any iodide; for if we add only sulphate of copper, not more than one-half of the iodine is got, the other half being set free, because no protoiodide of copper exists.

Disulphuret of Copper.  $\text{Cu}_2\text{S} = 79.4$ .

This is a native ore, and is formed artificially by heating a mixture of 3 parts of sulphur and 8 parts of copper filings. Copper pyrites is  $\text{Cu}_2\text{S} + \text{Fe}_2\text{S}_3$ .

Sulphuret of copper is also found combined with those of lead, silver, antimony and arsenic, as grey copper ore; of which there are several varieties. In these, the tersulphurets of antimony and arsenic play the part of acids, while the proto-sulphurets and disulphurets of iron, lead, silver and copper, are the basic ingredients. There are generally 4 eqs. of base to 1 of acid, and the two sets of sulphurets are variously combined.

A selenide of copper, combined with selenide of silver, also occurs, but it is rare.

The best antidote to the preparations of copper is white of egg, which forms with oxide of copper an inert compound.

47. LEAD.  $\text{Pb} = 103.7$ .

This valuable metal chiefly occurs combined with sulphur, forming the mineral galena, or lead-glance, from which all the lead of commerce is obtained. It is also met with as carbonate, sulphate, phosphate, and arseniate of oxide of lead. The galena is roasted to expel the sulphur and oxidise the lead, and the oxide is heated with charcoal to reduce the metal; indeed, a good deal of lead is obtained by heating the ore alone in a reverberatory furnace, where it is partly converted into sulphate of lead, and partly into oxide. Both of these act on undecomposed sulphuret, yielding sulphurous acid and metallic lead: thus  $2\text{PbO} + \text{PbS} = \text{SO}_2 + \text{Pb}_3$ ; and,  $\text{PbO}, \text{SO}_3 + \text{PbS} = 2\text{SO}_2 + \text{Pb}_2$ . Almost every variety of galena contains silver, which is concentrated, as its proportion is but small, and finally extracted, by a process to be described under silver.

Lead has a bluish-grey colour, and high lustre, but soon tarnishes. Its Sp. G. is 11·381. It is malleable, ductile, soft, and flexible, but of inferior tenacity. It melts at about 612°. When heated in air it is rapidly oxidised, and according to the heat, yields protoxide, or red oxide. The grey matter that forms on the surface of melted lead is a mixture of metal and protoxide.

Lead, when exposed to the action of air and moisture, is rapidly corroded, and particularly when in contact with pure or rain-water, forming a white crust of carbonate, which is highly poisonous. The oxygen and carbonic acid are absorbed from the air. This renders lead quite improper for pipes or cisterns, where rain-water, or very soft water is to be kept in them ; but Dr. Christison has shown that lead is protected by the presence of a minute quantity of saline matter, particularly sulphates and bicarbonate of lime, and as these exist in hard-water, or even in such water as that of Edinburgh, in sufficient quantity, lead may be safely used in such cases, as it is not corroded, the surface becoming covered with an insoluble film, which protects the mass of the metal.

Lead is precipitated from its solutions in the metallic state by other more highly positive metals, such as zinc. A piece of zinc, in a solution of 1 part of acetate of lead in 16 of water, to which a few drops of acetic acid have been added, forms a beautiful deposit of lead in large shining crystals, which grows in size for several hours. This was formerly called the *Arbor Saturni*.

Lead is a most useful metal, not only in itself, but as an ingredient in pewter, solder, and other important alloys.

#### LEAD AND OXYGEN.

##### a. Protoxide of Lead. $PbO = 111\cdot7$ .

Prepared by heating lead in air till it is entirely converted into a yellow powder which is the protoxide, often called *massicot*. When partially fused, as in the process of cupellation, it is called *litharge*. It is a heavy, insoluble, yellow or reddish powder, which is a powerful base, and forms with acids the salts of lead, which are generally colourless, and have a sweet taste. It has a strong tendency to form basic salts, such as the sub-acetate, which are alkaline, and attract carbonic acid from the air, forming the insoluble carbonate of lead. Such basic lead salts form a most delicate test for carbonic acid in air or gases. Their solutions give with potash a white hydrate, soluble in excess ; with carbonates, a white carbonate, which is the paint, white lead ; with sulphates, or sulphuric acid, a white insoluble sulphate ; with iodide of potassium, a bright yellow iodide of



sulphuret. Lead is very easily recognised in solution by the combination of the two tests of sulphuric acid and sulphuretted hydrogen, or iodide of potassium and sulphuretted hydrogen.

b. Sesquioxide of Lead.  $\text{Pb}_2\text{O}_3 = 231.4$ .

Is formed when solution of hypochlorite of soda is added to protoxide of lead dissolved in caustic soda. It is a reddish yellow insoluble powder, resolved by acids into protoxide and oxygen.

c. Peroxide of Lead.  $\text{PbO}_2 = 119.7$ .

Prepared by acting on red oxide of lead (see below) with dilute nitric acid, which dissolves protoxide, and leaves peroxide of lead as a puce-coloured insoluble powder. It is also formed when litharge is fused with chlorate of potash at as low a heat as possible; and when chlorine is passed through a solution of acetate of protoxide (sugar of lead). Here,  $2\text{PbO} + \text{Cl} = \text{PbCl} + \text{PbO}_2$ . The peroxide yields oxygen when heated, or when acted on by acids, which combine with protoxide, liberating oxygen. Peroxide of lead has weak acid properties when melted with potash or soda, the fused mass when dissolved in a little hot water, deposits, on cooling, crystals of plumbate of the alkali. Plumbate of potash is  $\text{KO}, \text{PbO}_2 + 3 \text{ aq}$ .

d. Red Oxide of Lead.  $\text{Pb}_3\text{O}_4 = 343.1$ .

This well-known pigment is formed when lead is exposed to a current of air at  $600^\circ$  or  $700^\circ$ . It is formed either of protoxide and peroxide,  $2\text{PbO} + \text{PbO}_2$ ; or of sesquioxide and protoxide,  $\text{Pb}_2\text{O}_3 + \text{PbO}$ . Acids resolve it into peroxide and protoxide. It is much used in the manufacture of flint glass, to give brilliancy and fusibility to the glass.

Chloride of Lead.  $\text{PbCl} = 139.2$ .

Is formed when hydrochloric acid or a soluble chloride is added to any solution of a salt of protoxide of lead.  $\text{HCl} + \text{PbO} = \text{PbCl} + \text{HO}$ . It is deposited in strong solutions as a white precipitate, sparingly soluble in cold water. It dissolves in hot water, and forms white needles on cooling. It is fusible below a red-heat, and forms on cooling a horny mass.

Lead forms several oxychlorides, one of which occurs in nature. It is  $\text{PbCl}, 2\text{PbO}$ . Another is formed by acting on galena with hydrochloric acid, dissolving the chloride of lead formed in water, and adding enough of lime-water to remove half the chlorine.  $2\text{PbCl} + \text{CaO} = \text{CaCl} + (\text{PbCl}, \text{PbO})$ . This, which like the preceding one is white, is used as a sub-

stitute for white lead. When 10 parts of litharge are heated with 1 of sal-ammoniac, a bright-yellow compound,  $\text{PbCl}, 7\text{PbO}$ , is formed : this is Turner's yellow, or patent yellow.

Iodide of Lead.  $\text{PbI} = 230.8$ .

Formed when hydriodic acid or a soluble iodide is added to a salt of protoxide of lead,  $\text{KI} + \text{PbO}, \text{NO}_3 = \text{PbI} + \text{KO}, \text{NO}_3$ . It forms a bright-yellow very sparingly soluble precipitate, which dissolves in hot water, forming a colourless solution ; and, on cooling, deposits beautiful yellow six-sided tables with the lustre of gold. Oxyiodides of lead also exist, and a singular compound of oxyiodide with carbonate of lead is formed, when tribasic acetate of lead is precipitated by a mixture of 1 eq. iodide of potassium and 4 eqs. of carbonate of potash. It is a blue powder, the formula of which is  $(\text{PbI}, \text{PbOI}) + 4(\text{PbO}, \text{CO}_2)$ .

Bromide of lead,  $\text{PbBr}$ , resembles the chloride.

Sulphuret of Lead.  $\text{PbS} = 119.7$ .

This is the native compound from which the lead of commerce is obtained. It is gray, and has a high metallic lustre, and is often found beautifully crystallised in cubes. By the action of fuming nitric acid, it is entirely converted into sulphate of lead.  $\text{PbS} + 4\text{NO}_3 = \text{PbO}, \text{SO}_3 + 4\text{NO}_2$ . It is formed by the action of sulphuretted hydrogen on the salts of lead, as a black powder.

ORDER 3.—METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY A RED-HEAT, OR NOBLE METALS.

48. MERCURY.  $\text{Hg} = 200$ .

This metal is distinguished from all others by its being liquid at ordinary temperatures. It is occasionally found in the metallic state : but its usual ore is the bisulphuret, known as cinnabar. From this it is obtained by distilling it in iron vessels with iron filings.

The appearance of mercury or quicksilver is well known. Its Sp. G. is  $13.545$  at  $47^\circ$  : but it contracts in freezing : and as a solid, its Sp. G. is  $15.612$ . It freezes at  $-39^\circ$ , and boils at  $620^\circ$ . When heated to its boiling point along with air, it slowly combines with oxygen, forming a red powder, which is peroxide of mercury, the *oxydum hydrargyri rubrum per se* of the older chemists. At a somewhat higher temperature the oxygen again separates from the metal. The uses of mercury for barometers, thermometers, mirrors, &c., are universally known.

## MERCURY AND OXYGEN.

 a. Protoxide of Mercury.  $\text{HgO} = 203$ .

To prepare it protochloride of mercury (calomel) is rapidly mixed with aqua potassæ in excess, by rubbing in a mortar; and the black powder formed is washed with cold water and dried in the dark.  $\text{HgCl} + \text{KO} = \text{KCl} + \text{HgO}$ . It is a black or dark olive powder, which is easily resolved into peroxide and metal,  $2\text{HgO} = \text{HgO}_2 + \text{Hg}$ ; and hence is difficult to keep. It is a feeble base, and forms with acids crystallisable salts, such as the acetate and nitrate. Its solutions are precipitated black by caustic alkalies; white (calomel) by hydrochloric acid, or a soluble chloride; and the metal is reduced by copper, phosphorous acid, or protochloride of tin.

 b. Peroxide of Mercury.  $\text{HgO}_2 = 216$ .

Is formed, as above mentioned, by the combined action of heat and air; but much more readily by dissolving mercury in nitric acid, evaporating to dryness, and heating the dry residue as long as any nitrous acid is given off. The peroxide is left in the form of a crystalline scaly powder, nearly black while hot, but of a light-red when cold. In this form it is often called red precipitate, a most absurd name, as it has not been prepared by precipitation, and when precipitated it appears as a yellow powder, which seems to be an allotropic form of the peroxide. It is a base, and forms salts with acids, which are apt to be decomposed by hot water, yielding insoluble yellow sub-salts and soluble super-salts. These salts give a yellow precipitate with caustic potash, a white with ammonia, and a fine scarlet with iodide of potassium; phosphorous acid, and the protochlorides of tin and copper, reduce the mercury to the metallic state.

Both the oxides of mercury, in their solutions, are precipitated black by sulphuretted hydrogen.

## MERCURY AND CHLORINE.

 a. Protochloride of Mercury.  $\text{HgCl} = 235.5$ .

SYN. *Calomel*.—Occurs sparingly as horn quicksilver in the mineral kingdom. May be prepared either by subliming a mixture of bichloride of mercury and mercury,  $\text{HgCl}_2 + \text{Hg}$ , which yields  $2\text{HgCl}$ ; or by adding hydrochloric acid or solution of common salt to a solution of protonitrate of mercury, when the protochloride is precipitated.  $\text{HgO}, \text{NO}_3 + \text{NaCl} = \text{NaO},$

$\text{NO}_5 + \text{HgCl}$ . It is a heavy white volatile powder, insoluble in water. It is blackened by alkalies. When first prepared, it is always contaminated with corrosive sublimate, and must be well washed with hot water before it is used as a medicine.

b. Bichloride of Mercury.  $\text{HgCl}_2 = 271$ .

**SYN. Corrosive Sublimate.**—This compound is formed when mercury is heated so as to burn in chlorine gas. It is prepared by subliming a mixture of bisulphate of peroxide of mercury with common salt.  $\text{HgO}_2, 2\text{SO}_3 + 2\text{NaCl} = 2(\text{NaO}, \text{SO}_3) + \text{HgCl}_2$ . Or it may be formed by dissolving peroxide of mercury in hydrochloric acid, when it is deposited in crystals. It is a heavy, translucent, crystalline, volatile solid, soluble in 20 parts of cold water, and in two parts of hot water. It has a very disagreeable acid, metallic taste, and is very poisonous. Its solution gives, with fixed alkalies, a yellow precipitate of peroxide; with ammonia, a white insoluble powder, called white precipitate; with sulphuretted hydrogen, first a white, and when the test is added in excess, a black precipitate of sulphuret; with iodide of potassium, a scarlet precipitate of periodide; and with protochloride of tin, a gray powder of metallic mercury.

The proper antidote to corrosive sublimate, as a poison, is albumen or white of egg, which forms with it an insoluble and inert compound.

Bichloride of mercury forms double salts with the chlorides of the more highly positive metals, which crystallise readily. It also yields several oxychlorides, which are formed when bicarbonate of potash acts on solution of corrosive sublimate. If a cold saturated solution of bicarbonate of potash be added gradually to 8 or 10 times its bulk of a cold saturated solution of sublimate, a light amorphous brick-red precipitate is formed. If there be only 3 or 4 volumes of the sublimate solution, the precipitate is crystalline, and red, purple, or violet; but both have the same composition. And if the solution of sublimate be only twice the bulk of the other, a jet black crystalline precipitate is formed, having the same composition. All three are  $\text{HgCl}_2 + 2\text{HgO}_2$ . But the two first yield with potash the yellow form, the third yields the red form of the peroxide.

If equal volumes of the solutions be mixed, golden-yellow scales, gradually becoming brown, are formed, which are  $\text{HgCl}_2 + 3\text{HgO}_2$ . This oxychloride also exists in the amorphous condition.

If the solution of sublimate be added to a large excess of that of the bicarbonate, brown crystalline crusts are obtained,

which are  $\text{HgCl}_2 + 4\text{HgO}_2$ . They yield the red peroxide with potash. But this oxychloride occurs amorphous and in golden scales, and then yields the yellow peroxide. The golden scales of this oxychloride are obtained by boiling either of the two others with water.

#### OXIDES AND CHLORIDES OF MERCURY WITH AMMONIA.

With ammonia, the peroxide of mercury forms a yellowish white compound, which has basic characters, and is called mercuramine. Its formula is either  $2\text{HgO}_2, \text{NH}_3, 2\text{HO}$ , or  $(\text{HgO}_2, \text{NH}_2\text{Hg}) \text{O}, \text{HO} + 2\text{HO}$ . It loses 2 eq. of water in vacuo, and the residue when heated, gives off 1 eq. more of water, leaving  $\text{HgO}_2, \text{NH}_2\text{Hg}, \text{O}$ . Its hydrate attracts carbonic acid powerfully, and forms definite salts with many acids. The chloride  $(\text{HgO}_2, \text{NH}_2, \text{Hg}) \text{Cl}$ , is formed as a heavy yellow powder, when corrosive sublimate is added to an excess of ammonia, and the precipitate boiled for some time in water.

When corrosive sublimate is added to excess of ammonia, white precipitate is formed. This is  $\text{HgCl}_2 + \text{Hg}_2\text{NH}_2$ . It corresponds to 2 eqs. of chloride of ammonium, in each of which 2 eqs. of hydrogen are replaced by 1 eq. of mercury. A heat of  $600^\circ$  converts it into a red crystalline compound,  $2\text{HgCl}_2 + \text{N}_2\text{Hg}_3$ .

When solution of corrosive sublimate is gradually added to a boiling solution of sal-ammoniac and ammonia, as long as the precipitate is redissolved, a compound is deposited on cooling in rhombohedral crystals, called fusible white precipitate. It appears to be  $(2\text{HgCl}_2, \text{Hg}_2\text{NH}_2) + 2\text{NH}_4\text{Cl}$ .

These compounds are interesting because in them mercury appears to take the place of some or even all of the hydrogen of ammonia. The formulæ, however, are very complex, whether we take, as has been done above, the old equivalent of mercury, 200, or the more modern one adopted by some chemists, namely 100, by which the peroxide and bichloride of mercury become protoxide  $\text{HgO}$ , and protochloride  $\text{HgCl}$ , while the protoxide above described becomes  $\text{Hg}_2\text{O}$ , and calomel  $\text{Hg}_2\text{Cl}$ . It is evident that the compounds of mercury are not yet thoroughly understood.

#### MERCURY AND IODINE.

##### a. Protoiodide of Mercury. $\text{HgI} = 327.1$ .

This compound is formed when iodine and mercury are rubbed together in the proper proportions, with a little alcohol,

which facilitates the combination ; or when iodide of potassium is added to solutions of protoxide of mercury ;  $\text{HgO} + \text{KI} = \text{KO} + \text{HgI}$ . It is a greenish-yellow, heavy, insoluble powder, which may be sublimed ; but it is apt to be decomposed by heat, and especially by light, into metallic mercury and periodide,  $2\text{HgI} = \text{HgI}_2 + \text{Hg}$ .

b. Biniodide of Mercury.  $\text{HgI}_2 = 454.2$ .

**Syn.** *Periodide of Mercury*.—Is obtained by rubbing together iodine and mercury in the proper proportions, with a little alcohol, and subliming ; or by adding iodide of potassium to a solution of corrosive sublimate.  $\text{HgCl}_2 + 2\text{KI} = 2\text{KCl} + \text{HgI}_2$ . It is an insoluble powder of the most brilliant scarlet colour, superior to that of vermilion, and equal to that of certain flowers, such as *Lobelia cardinalis*, *Salvia splendens*, and some varieties of *Pelargonium* : but unfortunately it loses part of its brilliancy, when exposed to light under certain circumstances. Although insoluble in water, it dissolves easily in an excess of either of its precipitants : a hot solution of nitrate of peroxide of mercury dissolves it, and on cooling, deposits it in beautiful red crystals.

The biniodide, when heated, undergoes a remarkable change : the red powder, which has an earthy aspect, passing into yellow crystals ; and when further heated, melting and subliming in large yellow rhombic tables. Either these, or the yellow crystalline powder first mentioned, sometimes retain their yellow colour pretty long ; but agitation, or friction, or the mere touch of a sharp point, at once causes them to become red, beginning at a point or points, and gradually changing throughout the mass. This is an allotropic modification, the result entirely of a new molecular arrangement ; for the composition of the red and yellow iodide is precisely the same. It forms crystallisable double salts with the alkaline iodides.

The bromides of mercury are very similar to the chlorides.

#### MERCURY AND SULPHUR.

a. Protosulphuret of Mercury.  $\text{HgS} = 216$ .

Formed by the action of sulphuretted hydrogen on diluted protonitrate of mercury. It is a black powder which, by heat, is resolved into metallic mercury and bisulphuret.

b. Bisulphuret of Mercury.  $\text{HgS}_2 = 232$ .

Occurs naturally, as cinnabar, and is the chief ore of mercury. It is formed by fusing sulphur with 6 parts of mercury, and

subliming ; or by pouring a solution of corrosive sublimate into an excess of hydrosulphuret of ammonia, when a black powder falls, which is to be dried and sublimed. When sublimed, the bisulphuret forms a dark-red crystalline mass, called cinnabar, which, when finely powdered, acquires a very fine red colour, and becomes vermillion.

The black powder obtained by triturating together equal parts of mercury and sulphur, and long known as Ethiop's mineral, is a mixture of sulphur with bisulphuret. It is to be observed, that the bisulphuret, like the biniodide, exists in two states, being sometimes black, and sometimes red.

#### 49. SILVER. $\text{Ag} = 108.$

This beautiful and useful metal is found in the metallic state ; also, as chloride and as sulphuret. It occurs also alloyed with gold, tellurium, antimony, copper, and arsenic. Almost all varieties of galena (the ore of lead) contain a small proportion of sulphuret of silver ; and in many places, it is found worth while to extract this silver from the lead smelted from the ore. The lead being melted is allowed to cool while stirred, when the pure lead crystallises sooner than the alloyed part. The crystals are ladled out in perforated ladles into another vessel. When  $\frac{3}{4}$  of the whole have thus been separated, the residue is placed in another vessel and again treated in the same way, when enough has accumulated. The more fusible parts becoming always richer in silver, while the less fusible are poorer. The latter are also, if necessary, again treated in like manner, and so on, till at one end of the series of vessels lead nearly free from silver, at the other lead very rich in silver, the latter of course in smaller quantity than the former, are obtained. The argentiferous lead in which the silver is thus concentrated, is brought to contain about 300 ounces of silver per ton, while the lead at the other end does not contain more than half-an-ounce per ton. The proportion in the original lead need not exceed 3 to 4 ounces per ton to admit of profitable extraction. It is not found advisable to push the process farther than the limit above stated, 300 ounces per ton. Of course, the more fusible lead of the latter stages contains silver enough to make it worth while to add it to fresh lead in the earlier stages. The silver of the argentiferous lead of the last operation is now extracted by cupellation : that is, by heating the alloy in a current of air, when the lead is oxidised, and the oxide is either absorbed by the cupel or porous cup ; or, on the large scale, is raked away to the side, while the silver remains as a bright metallic globule or button. The beautiful method, above

briefly described, of concentrating the silver in lead by crystallising out the lead, was devised by Mr. Pattison, of Newcastle. From the ore in which silver occurs as metal, it is extracted by amalgamation with mercury; and the amalgam being distilled, leaves pure silver.

Silver has a fine white colour and high lustre. It is highly malleable and ductile, and, when pure, is a soft metal. Its Sp. G. is 10·5; it melts at a full red-heat, and when melted in open vessels, it absorbs a considerable quantity of oxygen, without apparently combining with it; and on consolidating, gives out the whole, causing the metal to assume a beautiful frosted aspect. The uses of silver are quite familiar. For the purpose of making coinage or silver plate, it is alloyed in this country with rather less than  $\frac{1}{12}$  of copper, which renders it much harder and fitter for wear.

When silver, as commonly happens, has been alloyed with copper, it is purified in several ways. 1. By dissolving the alloy in nitric acid, and adding common salt, which throws down the silver as chloride; and from this the metal is separated (see below). 2. By dissolving the alloy in oil of vitriol, with the aid of heat, and acting on the hot solution with metallic copper, which precipitates the silver as metal, the copper taking its place in the solution. In both processes, the small quantity of gold usually present in commercial silver, is left by the acid as a black powder, when the silver and copper are dissolved; and its extraction generally covers the whole expense of the purification of the silver, leaving, besides, a profit to the purifier.

The proportion of silver in any alloy is ascertained, or the assay of silver made in two ways. 1. The alloy is melted with excess of lead and cupelled, when the silver is left. The less silver in the alloy the more lead must be added. The copper usually present in commercial silver, is oxidised and the oxide dissolved by the litharge and absorbed by the cupel, which is formed of bone-earth with a little wood ashes, and is very porous. 2. The alloy is dissolved, say 10 grains of it, in nitric acid, and the silver exactly precipitated by a solution of salt, of such strength that 1000 grains of it precipitate precisely 10 grains of pure silver. The solution of salt is added till it ceases to cause a precipitate, and the quantity used indicates the silver present in 10 grains of alloy. Thus, if 925 grains of salt solution just suffice to precipitate the silver in 10 grains of alloy, the proportion of silver is 9·25 grains in 10 of alloy; or 925 in 1000, which is the composition of our standard silver the remainder, 75 parts in 1000, being copper. For the minute details of these processes, and of all the necessary



precautions, the reader is referred to works on the subject of assaying.

Oxide of Silver.  $\text{AgO} = 116$ .

This, the only important oxide of silver, is obtained by dissolving silver in nitric acid, and adding caustic potash, when the oxide is precipitated as a brown powder. It may also be formed by boiling the moist recently prepared chloride with very strong potash, when it appears as a very dense pure black powder. It is a base, and neutralises all acids, forming salts, most of which are insoluble, or sparingly soluble. The oxide is reduced to the metallic state by a red-heat. Its solutions are easily recognised. They give, with caustic fixed alkalies, a brown precipitate; with ammonia, a similar one, soluble in the slightest excess; with hydrochloric acid, or any soluble chloride, the white curdy precipitate of chloride of silver, insoluble in water and acids, but soluble in ammonia; and with sulphuretted hydrogen, a dark-brown, nearly black precipitate of sulphuret. Silver and all its compounds are very sensitive to sulphuretted hydrogen, which blackens them. Most of the compounds of oxide of silver are very soluble in ammonia; and all the compounds of silver are darkened by the action of light, a property which is applied to useful purposes in the Daguerréotype, Calotype, and other photographic methods. Oxide of silver is reduced to the metallic state from its solutions by copper, zinc, and several other metals. When mercury is used, there is formed a beautiful arborescent crystallisation of an alloy of silver and mercury, called *Arbor Dianæ*.

When precipitated oxide of silver is acted on by ammonia a dark powder is formed, which fulminates violently when heated or by friction. Its composition is not exactly known; but it probably contains a compound of silver with nitrogen.

Silver is said to form a deutoxide and a peroxide, but these compounds present no features of interest, and are doubtful.

Chloride of Silver.  $\text{AgCl} = 143.5$ .

Is found in the mineral kingdom as horn silver; and is formed whenever oxide of silver comes in contact with chlorine, hydrochloric acid, or a soluble chloride.  $\text{AgO} + \text{HCl}$  (or  $\text{MCl}$ )  $= \text{AgCl} + \text{HO}$  (or  $\text{MO}$ ). It then forms a heavy white curdy precipitate, quite insoluble in water and acids, but soluble in ammonia. Hence, a solution of silver is a most delicate test for hydrochloric acid, or chlorides. The chloride melts at a heat below  $600^\circ$ , and, on cooling, forms a translucent horny mass. The freshly precipitated chloride is very sensitive to light, and this is the foundation of Talbot's Calotype.

To reduce the chloride to the metallic state, several methods are followed. 1. It is covered with water acidulated with sulphuric acid, and a rod of zinc is introduced, which gradually reduces the whole mass of chloride.  $\text{AgCl} + \text{Zn} = \text{Ag} + \text{ZnCl}$ . The silver is digested in dilute sulphuric acid, washed, dried, and fused. 2. The dried chloride is fused with carbonate of potash; when carbonic acid and oxygen are given off, chloride of potassium is formed, and metallic silver collects as a button in the bottom of the crucible. In this process the effervescence is troublesome: and if the heat be not high enough, the silver remains disseminated in the mass; while, if the heat be too high, the crucible is corroded, and the silver flows into the fire. Hence this process, although it succeeds in experienced hands, is very apt to fail in those of beginners, for which reason I have proposed the following. 3. The freshly precipitated chloride, while still moist, is boiled with very strong caustic potash, till it is converted into black oxide of silver entirely, or in great part. The oxide is then heated with a little pearlash and borax, and yields a button without any risk of failure. The oxide thus prepared, answers admirably for making pure nitrate of silver, as diluted nitric acid dissolves it instantly, leaving undissolved any undecomposed chloride. The action of the potash in the two last processes is very simple:  $\text{AgCl} + \text{KO} = \text{KCl} + \text{AgO}$ . 4. Lastly, the moist chloride is boiled with caustic potash and sugar, by which it is quickly reduced to the metallic state.

Iodide of Silver.  $\text{AgI} = 235.1$ .

Formed under the same circumstances as chloride of silver, which it resembles. It is a yellowish-white insoluble powder; insoluble in water, and nearly so in ammonia. It is very sensitive to light, and a film of iodide of silver is the substance which receives the impressions on the silver plates of the Daguerriotype.

The bromide of silver is very similar to the chloride.

Sulphuret of Silver.  $\text{AgS} = 124$ .

Occurs as a mineral, silver glance, and is formed by the action of sulphuretted hydrogen on oxide of silver, or indeed on silver itself, or any compound of it whatever. Polished silver is instantly tarnished by the minutest trace of sulphuretted hydrogen, so that coal-gas which contains a mere trace of that gas, cannot be used in silversmiths' shops. It would appear that the affinity of silver for sulphur is very powerful. The sulphuret is easily obtained by melting silver with an equivalent proportion

of sulphur. It can be cut with a knife. It is found also in nature, combined with tersulphide of antimony, forming red silver ore, in which the antimony is often partially replaced by arsenic.

50. GOLD.  $Au = 197$ .

This metal is found native, either pure or alloyed with silver and tellurium. Gold is seldom found in situ in gold districts, but sometimes occurs in quartz veins. In general, the rocks originally containing it, which are generally of the grauwacke kind, have been charged with gold near the surface, and, possibly from the presence of this and other metals, the upper parts of the beds have been long ago disintegrated by the action of the weather, and the gold carried down by the waters to the lower levels. Hence, in the Ural, in the old gold workings of America, in California, and in Australia, the extraction of gold is a mechanical operation, known as gold washing. Large nuggets are scarce, as are also the large masses of quartz traversed by numerous veins of gold of which we hear; by far the greater part of the gold is in the form of fine gravel or sand. Gold is very universally found all over the world, especially in districts where the older formations form the hills. In most countries of Asia and Africa gold is found, and has been from time immemorial; there are gold mines in Hungary and Transylvania, where, however, the gold is often found combined with tellurium and other metals; and in early ages there were rich gold mines, now exhausted, in France, Great Britain, Ireland, and almost all European countries. Even now, gold is to be found in the sands brought down by most rivers, and in some parts of Europe these sands are washed for it. In general, however, they are too poor to pay, unless where labour is very cheap. One form of iron pyrites has gold disseminated in it; it is called auriferous pyrites, and is wrought for gold, the metal being extracted by amalgamation with mercury. Native gold often contains a little silver. When combined with much silver, it is purified by quartation; that is by fusing it with so much silver, that the gold does not exceed one-fourth of the mass, and then acting on the alloy by nitric acid, which dissolves the silver, and leaves the gold as a black or brown powder, which, when fused, assumes the peculiar yellow colour of gold.

Gold is distinguished by its pure yellow colour, high metallic lustre and great density. Its Sp. G. is 19.3. It is the most ductile and malleable of all metals: and it melts in a strong red- or white-heat. From its feeble affinities, gold does not readily

tarnish, and may be heated for any time without change, except when it is exposed to a strong electric spark, when it burns with a green light. No single acid dissolves it; but it is easily dissolved by chlorine and nitrohydrochloric acid, or aqua regia, chlorine being apparently the solvent in both cases.

## GOLD AND OXYGEN.

The oxides of gold can only be obtained by indirect means.

a. Protoxide of Gold.  $\text{AuO} = 205$ .

Formed by the action of cold potash on protochloride of gold. It forms a green precipitate, which is soon resolved into teroxide and metallic gold. Ammonia converts it into fulminating gold, which probably is, or contains, a nitride of the metal.

b. Teroxide of Gold.  $\text{AuO}_3 = 221$ .

Obtained by adding magnesia to a neutral solution of terchloride of gold, as a yellow hydrate, which at  $212^\circ$  loses its water and becomes black. It is a very feeble base, having a tendency to combine with bases rather than with acids. It is therefore called auric acid. The aurate of potash forms yellow crystals, which are  $\text{KO}, \text{AuO}_3, 6 \text{ aq.}$  When acted on by ammonia it yields fulminating gold, a very dangerous compound, already mentioned. Its precise composition is not known, its explosive tendencies rendering its examination very difficult. A binoxide of gold,  $\text{AuO}_2$ , is supposed to exist, and to be formed as a purple powder when gold is burned by the electric spark.

## GOLD AND CHLORINE.

a. Protochloride of Gold.  $\text{AuCl} = 232.5$ .

Formed by exposing the terchloride to a heat of  $600^\circ$ . It is a yellow insoluble powder, which, by boiling in water is changed into metallic gold and terchloride.  $3\text{AuCl} = \text{Au}_2 + \text{AuCl}_3$ .

b. Terchloride of Gold.  $\text{AuCl}_3 = 303.5$ .

This, the usual form in which gold is dissolved, is obtained when gold is acted upon by aqua regia or by chlorine. It forms, when evaporated sufficiently, ruby-red crystals, which are deliquescent. The solution is yellow. It is reduced to the metallic state by many deoxidising agents, such as proto-sulphate of iron, formic acid and formiates, &c., &c.; and when the reduction takes place in a diluted solution, the metallic

gold appears as a blue powder as long as it is suspended in the liquid. Deoxidising agents probably act by decomposing water, the hydrogen of which deprives the gold of chlorine. Terchloride of gold is also reduced directly by the action of hydrogen, phosphuretted hydrogen, and metals. When heated it is first reduced to protochloride and afterwards to metallic gold.

When solution of protochloride or sesquichloride of tin is added to solution of gold, a purple precipitate is formed, long known as the purple of Cassius, and used for staining glass of the beautiful red colour seen in some of the Bohemian glass ware, and for painting on china a fine rose-colour and pink. Its composition is not known with certainty, but it contains gold, tin, and oxygen, probably as  $\text{AuO}, \text{SnO}_2 + \text{SnO}, \text{SnO}_2, 4 \text{ aq.}$

The iodides of gold are in composition analogous to the chlorides. The sulphuret, formed by the action of sulphuretted hydrogen on the terchloride, is a black powder, supposed to be tersulphuret,  $\text{AuS}_3$ .

#### 51. PLATINUM. $\text{Pt} = 98.7$ .

This metal, like gold, is found in the metallic state, but always alloyed with other metals, and generally mixed, as the ore of platinum, in the form of sand, with gold, silver, and other minerals in small proportion. The purification of platinum is a tedious operation, too difficult to be described here in a few words. But the essential parts of the process are the dissolving the platinum ore in aqua regia : the precipitating the platinum as a double chloride of ammonium and platinum ; and the igniting of this salt, which leaves pure platinum in a spongy state, containing, perhaps, a trace of iridium. The double chloride may also be reduced by the action of zinc and diluted sulphuric acid, when the platinum is obtained as a dense black powder. Spongy platinum is rendered malleable by being first exposed to powerful pressure, and then heated and hammered till it is rendered dense and workable. Or it may be fused before the oxyhydrogen blowpipe, being quite infusible in the furnace.

Pure platinum resembles silver, but is not so white. Its density is about 21.5, and it is both malleable and ductile, particularly the latter. It is not melted by any furnace-heat, nor acted on by air and heat together : hence its extreme utility to the chemist. When ignited with caustic alkalies, however, it is oxidised and corroded ; and care should be taken never to heat any metal, nor any mixture likely to yield a metal, especially a fusible one, in vessels of platinum, as it readily forms alloys, and is much injured in consequence. Platinum vessels

may be used, however, for the reduction of such metals as aluminium, glucinium, uranium, and some others by potassium. The proper solvent of platinum is chlorine or aqua regia, but it dissolves less easily than gold.

One of the most important properties of platinum is its power of causing gases to enter into combination. When a current of hydrogen gas plays on spongy platinum or platinum powder in the air, combination between the hydrogen and oxygen takes place at the surface of the platinum, and the heat developed is sufficient to make the metal red-hot. The red-hot metal, then acting like any other red-hot body, sets fire to the hydrogen. This power is present even in solid polished platinum; for if a perfectly clean plate of platinum be introduced into a mixture of oxygen and hydrogen, it will cause them to combine, and may, by becoming red-hot, even produce explosion. But the power is seen in greatest perfection in the black powder of platinum; and Döbereiner has shown that this powder contains within its pores about 250 times its volume of oxygen, which, as the pores do not exceed  $\frac{1}{4}$  of the powder, must occupy 10 more than  $\frac{1}{1000}$  of its bulk as gas, and must be denser than water. This explains the action on hydrogen. In the case of the polished metal it is supposed that the particles of the gases, which repel each other, are attracted by the metal, and consequently, on its surface, come within the sphere of affinity. The power of platinum, by virtue of the oxygen in its pores, rapidly oxidises the vapour of alcohol into acetic acid, &c.; and the smallest portion of this powder introduced into a mixture of oxygen and hydrogen causes instantaneous explosion.

#### OXIDES OF PLATINUM.

Platinum appears to form a green protoxide  $\text{PtO}$ , and a rust-coloured binoxide,  $\text{PtO}_2$ , which, when anhydrous, is nearly black; but these compounds are even more prone to change than the oxides of gold, and the binoxide is hardly to be obtained pure, owing to its tendency to combine with the alkalis used to precipitate it. Its compounds with potash and soda crystallise. The latter is  $\text{NaO}, 3\text{PtO}_2, 6 \text{ aq.}$  Those with the other bases are insoluble. Both oxides are prepared from the chlorides.

#### PLATINUM AND CHLORINE.

a. Protochloride of Platinum.  $\text{PtCl} = 134.2$ .

Prepared by heating the bichloride to  $450^\circ$ , when the protochloride is left as a greenish-gray insoluble powder. This

chloride enters into combination with ammonia, and the compound, under certain circumstances, gives rise to several very remarkable organic or quasi-organic bases, of which platinum is an element.

b. Bichloride of Platinum.  $\text{PtCl}_2 = 169.7$ .

This, the usual soluble salt of platinum, is best made by dissolving spongy platinum in aqua regia, and gently evaporating to the consistence of syrup, when on cooling the whole forms a crystalline brownish-yellow mass, very soluble in water. The solution of platinum is characterised by yielding metallic platinum as a black powder when acted on by zinc and diluted sulphuric acid; and by giving with salts of potash and of ammonia a sparingly soluble yellow double chloride, which is also reduced by zinc and sulphuric acid.

The double salts of bichloride of platinum with more positive chlorides are important. Those of the alkaline metals have the general formula,  $\text{MCl}, \text{PtCl}_2$ . Those of potassium and ammonium are isomorphous, and they are both pale yellow, sparingly soluble salts. The ammonium-salt is used to yield spongy platinum when heated, or platinum-black by the action of zinc and diluted sulphuric acid. It is also the form in which ammonia is usually determined, being quite insoluble in a mixture of alcohol and ether. The sodium salt is soluble and forms fine aurora-red tabular crystals, soluble also in alcohol and ether.

The tendency of the bichloride to form double salts is not confined to the ordinary metallic chlorides, but extends to the chlorides, or hydrochlorates, of all the organic bases. The double salts are in almost every case crystallisable, and when formed can be easily purified. When heated, they leave only platinum, from which their composition and equivalent can be calculated, if the amount of carbon, hydrogen and nitrogen in the base be previously known. This method has been of the utmost use in organic chemistry.

When the amount of nitrogen in organic compounds is to be ascertained, they are ignited with a mixture of hydrates of soda and lime, in a long tube, by which means the nitrogen is expelled in the form of ammonia. This is condensed by hydrochloric acid in a proper apparatus, and to the liquid bichloride of platinum is added in excess, the whole evaporated to dryness, and the residue well washed with alcohol and ether, when platinumchloride of ammonium is left, which is dried and ignited. The weight of the platinum left indicates the amount of nitrogen in the body analysed. As the platinumchloride is  $\text{NH}_4\text{Cl}, \text{PtCl}_2$ ,

it is evident, that every eq. of nitrogen in the substance analysed forms 1 eq. of that salt, and is represented by 1 eq. of platinum: so that 99 parts of platinum represent 14 of nitrogen.

It may here be mentioned, that by the action of ammonia on the chlorides of platinum, a number of remarkable complex bases have been obtained by Gros, Reiset, Raewsky and Gerhardt, containing the elements of ammonia or amidogen with platinum or chloride of platinum. These compounds are more fully described in the Organic Chemistry.

The iodides and sulphurets of platinum correspond in composition to the chlorides, but are of no practical interest. The iodides are very dark-coloured, so that the addition of iodide of potassium to a solution of platinum produces a very intense reddish-brown colour, gradually becoming nearly black.

#### 52. IRIIDIUM. Ir = 99.

This is one of the metals which accompanies platinum. It occurs combined with osmium, alloyed with a large proportion of platinum, and occasionally nearly pure, but still containing platinum. Specimens have been found of Sp. G. 23 to 26, indicating iridium as the heaviest of all metals. It is also the most infusible, the hardest, and that which resists best the action of acids. These latter properties would render it most valuable if it could be wrought, but as yet it has proved refractory. It is remarkably analogous to platinum, from which it chiefly differs in the darker colour of its chloride, and of the double chlorides which it forms with potassium and ammonium. The latter occurs in very dark-red octohedral crystals, nearly black, which when heated, leave metallic iridium, very similar to spongy platinum, and acting in the same way with hydrogen.

Iridium forms 4 oxides and 4 chlorides, which are little known. They have different colours; hence the name iridium, from iris, the rainbow. The oxides are  $\text{IrO}$ ,  $\text{Ir}_2\text{O}_3$ ,  $\text{IrO}_2$ , and  $\text{IrO}_3$ , and the chlorides correspond to them.

#### 53. OSMIUM. Os = 99.6.

This metal is found associated with iridium, constituting a small part of the ore of platinum, which is insoluble in aqua regia. When this residue is acted on at a red-heat, by nitric acid, both the metals are oxidised, and the mass being distilled with sulphuric acid, yields osmic acid,  $\text{OsO}_4$ , which condenses in fusible crystals. From the acid, the metal may be obtained by the action of reducing agents, as a black powder, which becomes metallic by friction.



Osmium is very infusible, and when it has been ignited in close vessels, may be heated in air without oxidation. It is chiefly remarkable for forming with oxygen a volatile acid, which has a pungent smell, like that of chlorine, and is very poisonous. It forms, altogether, 5 oxides,  $\text{OsO}$ ,  $\text{Os}_2\text{O}_3$ ,  $\text{OsO}_2$ ,  $\text{OsO}_3$ , and  $\text{OsO}_4$ ; 4 chlorides and 4 sulphurets, corresponding to the 4 first oxides.

Klaus has lately discovered, in the residue of platinum ore, along with iridium and osmium, a new metal which, from the red colour of its compounds, he calls ruthenium. It appears to be analogous to iridium, but has hitherto been little examined.

#### 54. PALLADIUM. $\text{Pd} = 53.3$ .

This metal is also one of those which occur in small quantity in the ore of platinum. It has lately been found rather more abundantly, alloyed with gold and silver. When the ore of platinum has been dissolved, and the solution rendered neutral by evaporation to dryness and resolution in water, a solution of bicyanide of mercury causes a flocculent, grayish-yellow precipitate of cyanide of palladium. When this is ignited, the palladium is left. It is rather more fusible than platinum, which it resembles in colour, lustre, and malleability, but is rather harder. Its Sp. G. is 11.3 to 11.8. From its not tarnishing, it is a valuable metal, and would be applied to many useful purposes, if it were less scarce. It is chiefly used by dentists in plates, as a substitute for gold. It is dissolved by nitric acid, but more easily by aqua regia.

Palladium forms two oxides: the protoxide,  $\text{PdO}$ , and the binoxide,  $\text{PdO}_2$ , both of which are black when anhydrous, and brown or yellow when hydrated. The binoxide forms fine red salts with acids, from which the palladium is precipitated as metal, by other metals, and by deoxidising agents in general.

There are two corresponding chlorides, a black protochloride,  $\text{PdCl}$ , and a dark brown bichloride,  $\text{PdCl}_2$ . The former yields with chloride of potassium a yellow double chloride, the latter a red one.

The protosulphuret of palladium,  $\text{PdS}$ , is easily formed by heating the metal with sulphur. It is a brittle, fusible, grey solid.

#### 55. RHODIUM. $\text{R} = 52.2$ .

This metal is also found, in small proportion, in the ore of platinum. It is separated from platinum, when both are in the state of chloride, by adding chloride of sodium, with which both the chlorides form double salts, of which the platinum salt is soluble, the rhodium salt insoluble, in alcohol. When purified,

the rhodium salt is dissolved in water, and the rhodium precipitated by metallic zinc. It appears as a black powder, which may be fused in a powerful wind furnace, and is then white and metallic, very hard, brittle, and of Sp. G. 11.

Rhodium is hardly dissolved by any acids, unless when alloyed with other metals. The best method of dissolving it is to fuse it with bisulphate of potash, when it forms a soluble double salt. Rhodium, from its great hardness, has been used to form the tips of metallic pens, which are said to last wonderfully.

It forms two oxides; a protoxide, and a sesquioxide,  $R_2O_3$ ; and probably two corresponding chlorides. The solution of the sesquichloride is of a fine red colour, and most of the salts of rhodium are either red or yellow.

The sulphuret of rhodium is bluish-grey, metallic, and fusible at a white-heat.

#### ALLOYS.

The compounds of metals with metals are called alloys, and many of them are extremely useful and important. The alloys into which mercury enters, as a component part, are called amalgams.

Fine solder is an alloy of two parts of tin and one of lead. It melts at  $360^\circ$ . Coarse solder, which melts at  $500^\circ$ , contains one part of tin and three of lead. Hard solder, for copper, is a compound of copper and zinc, the latter metal being in excess.

Pewter is composed of tin, with a little antimony, copper, and bismuth; the inferior kinds contain a good deal of lead.

Newton's fusible metal is composed of 8 parts of bismuth, 5 of lead, and 3 of tin. It melts below  $212^\circ$ , and as it expands in cooling, takes very delicate impressions. It is used to form moulds for electrotyping, and also to take copies of dies in different stages of their progress, that the artist may judge of his work.

Type metal is an alloy of 3 parts of lead, and 1 of antimony, along with a certain proportion of tin.

Bronze is composed of about 90 parts of copper to 10 of tin; bell-metal and gong-metal, of 80 parts of copper to 20 of tin. Speculum metal, for telescopes, is formed of 2 parts of copper and 1 of tin, with a little arsenic.

Brass is an alloy of copper and zinc; the best contains 4 parts of copper and 1 of zinc; and when the proportion of zinc is increased, we have tombac, Dutch gold, and pinchbeck.

Tutenague, or white copper, as it is called in China, or German silver, as it is now called in Europe, is an alloy of copper, zinc, and nickel; the finer kinds containing most nickel.

Steel appears to form valuable alloys with a very small pro-

portion of some other metals. With a little silicon and aluminium, it yields a metal equal to the Indian wootz ; and with small quantities of silver, platinum, rhodium, palladium, and even iridium and osmium, alloys of prodigious hardness and toughness are obtained.  $\frac{1}{500}$  part of silver is sufficient to effect a marked improvement. Mr. Morries Stirling has recently introduced a number of valuable alloys of iron with tin, zinc, antimony, and other metals. It would appear that the number of possible alloys is most unlimited, and that they possess every variety of property. Some of the new alloys are very sonorous, equal to bell-metal ; others are adapted for cutting instruments, others for speculum metal, and all these results, and many more, have been obtained with iron, a metal formerly supposed to form no alloys. The subject is a most important one. Mr. Stirling has also shown that mixtures of cast iron and malleable iron have most valuable properties, being hard and yet tough, while malleable iron, with a very little of some other metal, acquires a high degree of hardness.

Standard silver, and standard gold, are alloys, with from  $\frac{1}{13}$  to  $\frac{1}{12}$  of copper, which much increases the hardness of these metals, without injuring their colour.

An amalgam of tin is used for silvering the backs of mirrors ; and an amalgam of 4 of mercury, 2 of bismuth, 1 of lead, and 1 of tin, is used for silvering the inside of hollow glass globes.

The amalgam used for exciting electrical machines is formed of 1 part of zinc, 1 of tin, and 2 of mercury.

The tendency of mercury to combine with gold and silver is made use of in extracting these metals from their ores. An amalgam of 1 part of gold, and 8 of mercury, is used in gilding brass.

It is probable that the best alloys are those which contain atomic proportions of their ingredients ; but this subject has been as yet little studied. Alloys are always more fusible than their least fusible ingredient, and they are commonly harder and more brittle than their elements. They are sometimes more dense, sometimes less dense than we should expect from the densities of the combining metals.

## SALTS.

The salts are a very important and useful class of compounds ; but our space will not allow us to describe them minutely, and we must be satisfied with a few general remarks, applicable to the whole class, and with a brief statement of the characters which distinguish the separate families of salts, as marked by

the acids they contain. We have already given, under the different metals, the characters of the different bases in their salts. Fortunately the analogies among the very numerous salts are so strong and well marked, that here, better than in any other department, minute details may be omitted.

When the term salt was first extended beyond sea-salt, the original type, it was applied to substances having similar properties, such as solubility, neutrality, and saline taste, with the property of crystallising. It was found, after a time, that salts were produced by the combination of acids with alkalies, or at least by bringing them together; and as sea-salt was obtained when soda and muriatic acid were mixed, it was supposed to be formed of these constituents, just as sulphate of soda was supposed to consist of sulphuric acid and soda.

But when, in process of time, it came to be known that sea-salt contained neither muriatic acid nor soda, it was found necessary, since it was impossible to deny the claim of sea-salt to rank as a salt, to admit two kinds or classes of neutral salts, one formed of an oxygen acid and an oxygen base; the other of a salt-radical and a metal. Thus, while sulphate of soda was  $\text{NaO}, \text{SO}_3$ , sea-salt was  $\text{NaCl}$ ; the former corresponding to the hydrated acid,  $\text{HO}, \text{SO}_3$ ; the latter to the hydrogen acid  $\text{HCl}$ . This, indeed, is the view which has for many years prevailed.

But it did not escape the sagacious mind of Davy, that according to this view, we give two different explanations of phenomena almost identical, and that a more truly philosophical view might be taken.

When hydrated sulphuric acid acts on soda, we have two marked phenomena: these are, the formation of a neutral salt and the separation of water. This is represented as follow:  $\text{NaO} + \text{HO}, \text{SO}_3 = \text{HO} + \text{NaO}, \text{SO}_3$ . Now, when hydrochloric acid acts on soda, we observe exactly the same phenomena—the formation of a neutral salt, and the separation of water; but the explanation is now different. It is  $\text{NaO} + \text{HCl} = \text{NaCl} + \text{HO}$ .

Davy showed that, in the latter case, but one explanation was possible—because the hydrogen could only come from the hydrochloric acid, and the oxygen from the soda; and he proposed so to view the former case as to bring it under the same explanation.

He pointed out, that we have no certainty that the hydrated sulphuric acid really contains water; or the sulphate of soda, oxide of sodium; and that, instead of the formula  $\text{HO}, \text{SO}_3$ , we might with better reason adopt the formula  $\text{H}, \text{SO}_4$  for the

acid, which would thus come to be considered a hydrogen acid, differing from hydrochloric acid only in containing a *compound* radical,  $\text{SO}_4$ , instead of a *simple* one  $\text{Cl}$ . But, in the first place, chlorine may not be really a simple body; and secondly, if it were so, we know that compound radicals exist, performing exactly the part which is here ascribed to the hypothetical body  $\text{SO}_4$ .

Thus, cyanogen,  $\text{Cy} = \text{C}_2\text{N}$ , with hydrogen, forms hydrocyanic acid,  $\text{HCy}$ , which acts on bases exactly as hydrochloric acid does, yielding a neutral salt, a cyanide and water,  $\text{MO} + \text{HCy} = \text{MCy} + \text{HO}$ .

Let us represent  $\text{SO}_4$ , by  $\text{Su}$ , and then we have  $\text{HSu} =$  hydrated or real sulphuric acid; and when it acts on soda,  $\text{NaO} + \text{HSu} = \text{NaSu} + \text{HO}$ . We have then:—

|                 | Chlorine.        | Cyanogen.        | Radical of Sulphuric Acid. |
|-----------------|------------------|------------------|----------------------------|
| Radical . . .   | $\text{Cl}$ . .  | $\text{Cy}$ . .  | $\text{Su}$                |
| Hydrogen Acid . | $\text{HCl}$ . . | $\text{HCy}$ . . | $\text{HSu}$               |
| Neutral Salt .  | $\text{MCl}$ . . | $\text{MCy}$ . . | $\text{MSu}$               |

In this form we see that, assuming sulphuric acid to be a hydrogen acid, the whole of its relations admit of being expressed as simply as those of hydrochloric acid. These two acids, and all acids analogous to either of them, come into the same category, and the same is true of their salts, all of which are considered compounds of metals with radicals, simple or compound. In this simple way we get rid of the absurdity of two different explanations for the same phenomena, and we arrive at the following general definition of an acid and of a salt:—

An acid is the hydrogen compound of a simple or compound radical, possessing the power of neutralising bases; and its general formulæ are,  $\text{HR}$ ,  $\text{HR}_2$ ,  $\text{HR}_3$ , &c.

A salt is the compound formed by replacing the hydrogen of an acid by a metal; and the general formulæ for salts are  $\text{MR}$ ,  $\text{MR}_2$ ,  $\text{MR}_3$ , &c.

This is the only view that can be taken in the case of the acids and salts of simple radicals; but in the case of compound radicals, we have already seen that another view is taken. For example, oil of vitriol is considered to be, not a hydrogen acid, but an oxygen acid united to water, and is called hydrated sulphuric acid,  $\text{HO}, \text{SO}_3$ ; and in its salts the water is supposed to be replaced by a metallic oxide,  $\text{MO}, \text{SO}_3$ .

In favour of this, the ordinary view, it is urged that dry sulphuric acid,  $\text{SO}_3$ , exists, and that, in contact with water, it produces hydrated sulphuric acid; in contact with bases,

sulphates. That, although oil of vitriol may be viewed as  $\text{H}_2\text{SO}_4$ , this view is improbable, because the body  $\text{SO}_4$ , the supposed radical, is unknown in a separate form, and that many undoubted oxygen acids exist containing no hydrogen, as carbonic, silicic, phosphoric, and chromic acids.

To these considerations it may be replied, that although the body  $\text{SO}_3$  exists, it is not truly an acid, and does not acquire acid properties until it has been in contact with water, and combined with it, that is, with hydrogen. That with ammonia,  $\text{SO}_3$  does not form sulphate of ammonia, but an entirely different compound. That, although the supposed radical  $\text{SO}_4$  is unknown in a separate form, this objection has little weight; first, because many compounds, universally admitted, are not known in the separate state; secondly, because the supposed compound may be obtained at any time, just as dry nitric acid,  $\text{NO}_5$ , long unknown in the separate form, has lately been obtained. That those oxygen acids which exist without hydrogen, such as dry sulphuric acid,  $\text{SO}_3$ , dry phosphoric acid,  $\text{PO}_5$ , carbonic acid,  $\text{CO}_2$ , silicic acid,  $\text{SiO}_3$ , and chromic acid,  $\text{CrO}_3$ , either have no acid properties till water is added, as in the case of  $\text{SO}_3$ , and  $\text{PO}_5$ , or possess very feeble and ill-marked acid properties, as in the case of carbonic and silicic acids, which cannot neutralise the alkalies, and form with them an almost unlimited number of compounds. That all those oxygen acids which possess in perfection the acid character, such as oil of vitriol, nitric acid, phosphoric acid in its active state, and the whole of the organic acids, invariably contain hydrogen in a form in which it is replaced by metals in the salts, or, according to the older view, water, which in the salts is replaced by a metallic oxide. Now, as in water,  $\text{HO}$ , and a metallic oxide,  $\text{MO}$ , the oxygen is the same, it is, even on that view, hydrogen which is replaced by metal when an acid is converted into a salt.

It may be added, that considerations derived from the phenomena of galvanic decomposition (Daniell), from the heat developed when bodies combine to form salts (Graham, Andrews), and from the molecular or atomic volume of acids and salts (Kopp), all concur to render it probable that oxygen acids are hydrogen compounds, not hydrates, and that oxygen salts contain a metal united to a radical, and not an oxide united to a dry or anhydrous acid.

On the whole, therefore, the simpler view, and that which admits of but one kind of acids, and one kind of salts, is, in the present state of our knowledge, to be preferred; but we give the formulæ according to both views, since we ought to be equally familiar with both. But it must be borne

in mind, that although the view here preferred has some advantages, it is not universally satisfactory, and that, like all such hypotheses, it is useful chiefly as a means of assisting us to classify and remember facts, and has no claim to be regarded as ascertained truth.<sup>1</sup>

We may even go further, and, excluding all notion of any binary arrangement in salts, and indeed in compounds generally, consider them to be compound units, in which no one arrangement is more probable than another. Thus, sulphate of potash would be represented, neither as  $\text{KO}, \text{SO}_3$ , nor as  $\text{K}, \text{SO}_4$ , but as  $\text{KSO}_4$ . The binary arrangements would then merely represent the more usual modes of decomposition, when electricity or chemical attraction is applied. Now, we know that most compounds may be made to undergo several different binary decompositions, all of which, it is plain, cannot represent the constitution of the compound, if that be binary. Thus, sulphate of potash may be so decomposed as to be resolved into sulphuric acid and potash,  $\text{SO}_3$  and  $\text{KO}$ ; or, as in the electric current, into potassium,  $\text{K}$ , and  $\text{SO}_4$ , the latter spontaneously resolving itself into  $\text{SO}_3 + \text{O}$ ; or, as when heated in hydrogen, into sulphuret of potassium,  $\text{KS}$ , and  $\text{O}_4$ ; besides other ways that may be conceived.

Yet it cannot be denied, that nature exhibits a strong tendency to a binary arrangement, and in innumerable cases, the bodies which unite to form a compound are easily obtained from it. We must, therefore, make use of this character as a guide and principle of classification, without seeking to make all facts bend to it.

Since salts are formed from acids by the replacement of the hydrogen of the acid by a metal, and since acids exist containing more than one equivalent of hydrogen (or of water) replaceable by metals (or metallic oxides), it is advisable to class the salts according to the acids from which they are derived, whether monobasic or polybasic.

Monobasic acids are those of which an equivalent forms a neutral salt with 1 eq. of base. The general formula of a monobasic acid, considered as a hydrogen acid, is  $\text{HR}$ , and its action on a protoxide is as follows;  $\text{HR} + \text{MO} = \text{HO} + \text{MR}$ ; so that  $\text{MR}$  is the general formula for a monobasic salt.  $\text{R}$ . stands here for the radical, which with hydrogen forms the acid.

On the other view, a monobasic oxygen acid is a hydrate containing 1 eq. of water and 1 eq. of dry or anhydrous acid, and the general formula is  $\text{HO}, \text{RO}_x$ ;  $\text{R}$  standing here for the combustible element of any oxygen acid, which may be united with 2, 3, or more eqs. of oxygen in the anhydrous,

acid. The action of such an acid on a base is as follows:— $\text{HO}, \text{RO}_x + \text{MO} = \text{MO}, \text{RO}_x + \text{HO}$ ; so that, on this view, the general formula for a monobasic neutral salt is  $\text{MO}, \text{RO}_x$ .

The most important oxygen acids of inorganic nature, are the following: sulphuric, sulphurous, nitric, hypochlorous, chloric, perchloric, iodic, phosphoric, arsenic, arsenious, chromic, boracic, silicic, and carbonic acids, the salts of which are now to be very briefly described. The salts formed by the monobasic hydrogen acids with simple radicals have been already described, under the respective metals, as chlorides, bromides, iodides, fluorides, sulphurets, &c.

#### SULPHATES.

General formula of neutral sulphates:  $\text{M}, \text{SO}_4$ , or  $\text{MO}, \text{SO}_3$ .  
General formula of bisulphates:  $\text{M}, \text{SO}_4 + \text{H}, \text{SO}$ ; or  $\text{MO}, \text{SO}_3 + \text{HO}, \text{SO}_3$ .

Of the sulphates, some are found native; some are very soluble, some sparingly soluble, some insoluble. All the soluble sulphates are recognised in solution by the test of nitrate of baryta, which causes a white precipitate of sulphate of baryta, insoluble in acids. All the insoluble sulphates, when fused with carbonate of soda, yield sulphate of soda, which may be recognised as above: or, when heated with charcoal, they yield sulphurets, which are easily known by their blackening the salt of lead. The action of charcoal on a sulphate is thus represented:  $\text{MO}, \text{SO}_3 + \text{C}_4 = 4\text{CO} + \text{MS}$ ; or,  $\text{M}, \text{SO}_4 + \text{C}_4 = 4\text{CO} + \text{MS}$ .

The sulphates of the weaker bases are decomposed by a white heat, but those of the stronger bases are not altered.

Some neutral sulphates exist in the anhydrous state,  $\text{MO}, \text{SO}_3$  or  $\text{M}, \text{SO}_4$ . Others occur combined with 1 eq. of what Graham calls constitutional water, requiring a red heat for its expulsion, and capable of replacement by another neutral sulphate and many occur with several equivalents of water of crystallisation.

Sulphate of potash crystallises in six-sided prisms and pyramids, which are anhydrous. Its formula is  $\text{KO}, \text{SO}_3$ , or  $\text{K}, \text{SO}_4$ .

Bisulphate of potash crystallises in fine needles, the formula of which is  $(\text{KO}, \text{SO}_3 + \text{HO}, \text{SO}_3)$ , or  $(\text{K}, \text{SO}_4 + \text{H}, \text{SO}_4)$ . It is a very acid salt, and is much used as a flux in mineral analysis.

Sulphate of soda, or Glauber's salt, forms large prisms, the formula of which is  $\text{NaO}, \text{SO}_3 + 10 \text{ aq.}$ ; or  $\text{Na}, \text{SO}_4 + 10 \text{ aq.}$  It is used as a laxative; and from this salt in its anhydrous state (prepared from sea-salt by the action of oil of vitriol), carbonate



of soda is manufactured by heating it with charcoal in a reverberatory furnace.

Sulphate of ammonia ( $\text{NH}_3, \text{HO}, \text{SO}_3$ ) or ( $\text{NH}_4, \text{SO}_4$ ), crystallises in the same form as sulphate of potash. With water of crystallisation it forms crystals of a totally different form,  $\text{NH}_4 \text{O} + \text{SO}_3 + \text{aq.}$

Sulphate of baryta, or heavy spar, occurs native in large tabular and also prismatic crystals. It is remarkable for its insolubility in water and acids. It is decomposed by ignition with charcoal, yielding sulphuret of barium, from which all the other compounds of barium may be obtained. It is anhydrous, and its formula is  $\text{BaO}, \text{SO}_3$ , or  $\text{Ba}, \text{SO}_4$ .

Sulphate of strontia, or celestine, also occurs native, and is very analogous to the preceding. It serves, when decomposed by ignition with charcoal, to yield all the compounds of strontium. Formula  $\text{SrO}, \text{SO}_3$ , or  $\text{Sr}, \text{SO}_4$ .

Sulphate of lime. This salt occurs native, as gypsum, selenite, and alabaster, the formula of which is  $(\text{CaO}, \text{SO}_3 + \text{HO}) + \text{aq.}$ ; or  $(\text{Ca}, \text{SO}_4 + \text{HO}) + \text{aq.}$  In the mineral anhydrite, it is anhydrous,  $\text{CaO}, \text{SO}_3$ , or  $\text{Ca}, \text{SO}_4$ . When heated to  $270^\circ$ , gypsum loses both its constitutional water, and its water of crystallisation, and falls in a fine powder, which is plaster of Paris; and which, when mixed with water, combines with it again, forming a solid compound, or setting, as it is called. Hence its use in moulding. Gypsum is also a very valuable manure. It is sparingly soluble in water, but its solution is precipitated copiously by salts of baryta.

Sulphate of magnesia, or Epsom salts, occurs in some springs, and is easily made by dissolving carbonate of magnesia in sulphuric acid. It is very soluble, and crystallises readily in four-sided prisms, the formula of which is  $(\text{MgO}, \text{SO}_3 + \text{HO}) + 6 \text{ aq.}$  It is much used as a laxative.

Sulphate of alumina does not crystallise, but it enters into the composition of crystallisable double salts, called alums. Its formula is  $\text{Al}_2\text{O}_3, 3\text{SO}_3$ , or  $\text{Al}_2, 3\text{SO}_4$ .

A subsulphate, or trisulphate of alumina occurs native as the mineral aluminite. Formula,  $\text{Al}_2\text{O}_3, \text{SO}_3 + \text{aq.}$

Sulphate of manganese forms pale-pink, or colourless crystals, of the formula  $(\text{MnO}, \text{SO}_3 + \text{HO}) + 4 \text{ aq.}$ ; or,  $(\text{Mn}, \text{SO}_4 + \text{HO}) + 4 \text{ aq.}$

Sulphate of iron (protoxide) or green vitriol. This well-known salt forms pale-green oblique prisms. Formula  $(\text{FeO}, \text{SO}_3 + \text{HO}) + 5 \text{ aq.}$ ; or  $(\text{Fe}, \text{SO}_4 + \text{HO}) + 5 \text{ aq.}$  It is used in the manufacture of fuming sulphuric acid, hence called oil of vitriol; in making ink; and very extensively in dyeing, and calico-printing. It is also much used in medicine.

Sulphate of the peroxide of iron does not crystallise, but forms crystallisable double salts. Formula  $\text{Fe}_2\text{O}_3, 3\text{SO}_3$ ; or,  $\text{Fe}_23\text{SO}_4$ .

Sulphate of zinc, or white vitriol, forms crystals exactly similar to those of sulphate of magnesia. Formula  $(\text{ZnO}, \text{SO}_3 + \text{HO}) + 6 \text{ aq.}$ ;  $(\text{Zn}, \text{SO}_4 + \text{HO}) + 6 \text{ aq.}$  It is much used in surgery, and is formed when zinc is dissolved in diluted sulphuric acid.

Sulphate of nickel forms emerald-green crystals of the same form as the preceding. Formula  $(\text{NiO}, \text{SO}_3 + \text{HO}) + 6 \text{ aq.}$ ; or,  $(\text{Ni}, \text{SO}_4 + \text{HO}) + 6 \text{ aq.}$

Sulphate of cobalt forms rose-red crystals of the same form as green vitriol. Formula  $(\text{CoO}, \text{SO}_3 + \text{HO}) + 5 \text{ aq.}$ ; or,  $(\text{Co}, \text{SO}_4 + \text{HO}) + 5 \text{ aq.}$

Sulphate of chromium does not crystallise, but forms crystallisable double salts. Formula  $\text{Cr}_2\text{O}_3, 3\text{SO}_3$ ; or,  $\text{Cr}_2, 3\text{SO}_4$ .

Sulphate of copper, or blue vitriol, forms azure-blue crystals, exactly of the same form as those of sulphate of manganese. Its formula is  $(\text{CuO}, \text{SO}_3 + \text{HO}) + 4 \text{ aq.}$ ; or  $(\text{Cu}, \text{SO}_4 + \text{HO}) + 4 \text{ aq.}$  With excess of ammonia it forms a deep violet-blue salt, the ammoniuret of copper, in which the water of crystallisation of blue vitriol, or a part of it, appears to be replaced by ammonia. Sulphate of copper is much used as an escharotic in surgery.

Sulphate of peroxide of mercury is formed as a crystalline powder, when mercury is boiled to dryness with sulphuric acid. Its formula is  $\text{HgO}_2, 2\text{SO}_3$ , or  $\text{Hg}, 2\text{SO}_4$ . It is used in the preparation of corrosive sublimate, and of calomel.

Sulphate of silver forms anhydrous crystals, having the same form as those of anhydrous sulphate of soda. Formula  $\text{AgO}, \text{SO}_3$ , or  $\text{Ag}, \text{SO}_4$ .

#### DOUBLE SULPHATES.

Of these there are two well-marked groups. The type of the first is sulphate of magnesia and potash; the type of the second is sulphate of alumina and potash, or alum.

1. When sulphate of potash and sulphate of magnesia are mixed in equivalent proportions, and the solution evaporated, crystals are deposited of a well-marked form, the formula of which is  $(\text{KO}, \text{SO}_3 + \text{MgO}, \text{SO}_3) + 6 \text{ aq.}$ ; or  $(\text{K}, \text{SO}_4 + \text{Mg}, \text{SO}_4) + 6 \text{ aq.}$  It appears to have been formed from sulphate of magnesia, by the substitution of  $\text{KO}, \text{SO}_3$ , for the constitutional  $\text{HO}$ , the 6 aq. remaining unchanged. It is but the type of a large group; for similar double salts may be formed with sulphate of potash, and the sulphates of zinc, nickel, cobalt, iron, copper, and manganese; and another series, of exactly the same form, may be obtained by substituting sulphate of ammonia for sulphate of

potash ; as, for example, in the double sulphate of magnesia and ammonia ( $\text{NH}_4\text{O}, \text{SO}_3 + \text{MgO}, \text{SO}_3$ ) + 6 aq.

2. Common alum, the type of the second group, is formed when sulphate of potash combines with sulphate of alumina, and its formula is  $(\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3\text{SO}_3) + 24 \text{ aq.}$  ; or  $(\text{K}, \text{SO}_4 + \text{Al}_2, 3\text{SO}_4) + 24 \text{ aq.}$  Now, this is also the type of a numerous group ; for the potash may be replaced by soda or ammonia, and the alumina may be replaced by the sesquioxides of iron, manganese, and chromium. The general formula of this group is  $(\text{MO}, \text{SO}_3 + \text{m}_2\text{O}_3, 3\text{SO}_3) + 24 \text{ aq.}$  ; M representing potassium, sodium, or ammonium, and m, aluminium, iron, manganese, or chromium. All the salts of this group, which are called alums, crystallise in octohedrons, and contain the same amount of water.

When we consider the facts above noticed, the circumstance that the sulphates of copper and manganese, with 4 eqs. of water of crystallisation, those of iron and cobalt with 5 eqs., and those of magnesia, zinc, and nickel with 6 eqs., respectively crystallise in the same forms, different for each group ; and when we reflect on the two remarkable groups of double sulphates just described, we cannot avoid the conclusion, that similarity of constitution is one main cause of similarity of crystalline form ; and this constitutes the doctrine of isomorphism, as at present understood and admitted. By similarity of constitution is meant, not only a likeness in the nature of the elements present, but a similar arrangement of those elements.

Thus, in common alum,  $\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3\text{SO}_3 + 24 \text{ aq.}$ , and in ammonia-iron alum,  $\text{AmO}, \text{SO}_3 + \text{Fe}_2\text{O}_3, 3\text{SO}_3 + 24 \text{ aq.}$  ; not only is ammonium (Am) analogous to potassium, and iron to aluminium, but the new elements occupy the same position as the original ones, as is shown by the formula.

#### SULPHITES.

The sulphites are recognised by their giving off the suffocating smell of sulphurous acid when acted on by a stronger acid. They have lately been studied by Muspratt, who has found that a very close analogy exists between the sulphites and the carbonates.

#### NITRATES.

The nitrates are easily prepared by the action of nitric acid on bases, on metals, or on carbonates. They are all decomposed by a red heat, and they all deflagrate with red-hot charcoal. In solution they are best recognised by adding sulphuric acid

and warming, which sets free the nitric acid, and then cautiously adding solution of green vitriol, which, at the line of junction of the two liquids, becomes black or red, according to the proportion of nitric acid, from its peculiar action on the protosalts of iron. The general formula of nitrates, in the anhydrous state, is  $\text{MO}, \text{NO}_5$ , or  $\text{M}, \text{NO}_6$ .

Nitrate of potash, nitre or saltpetre, is found as an efflorescence on the soil in hot climates, and may be formed artificially in nitre-beds. The essential conditions are the presence of a fixed base, particularly potash; and of decaying organic matter, or some other source of ammonia, which is oxidised, producing nitric acid and water; and the acid then unites with the base. The ammonia  $\text{NH}_3$ , with 8 eqs. of oxygen from the air, gives rise to nitric acid and water,  $\text{NO}_5 + 3\text{HO}$ , or  $\text{H}, \text{NO}_6 + 2\text{HO}$ . There is no reason to believe that the nitrogen of the atmosphere is ever oxidised, or contributes to nitrification; and the minute trace of nitric acid, sometimes observed in the rain of thunder-storms, has in all probability been formed from the ammonia of the atmosphere.

Nitre crystallises in six-sided prisms. It is much used in making gunpowder, and as an oxidising agent; also in the manufacture of nitric acid. Formula,  $\text{KO}, \text{NO}_5$ , or  $\text{K}, \text{NO}_6$ .

Nitrate of soda is formed precisely in the same way, where soda is the base present in the soil, and occurs in immense quantities in some parts of South America. It crystallises in rhombohedrons. It is much used in the manufacture of sulphuric and nitric acids, but does not answer for gunpowder. Formula,  $\text{NaO}, \text{NO}_5$ , or  $\text{Na}, \text{NO}_6$ .

Both nitre and nitrate of soda are used as manures: and it is still uncertain whether the acid of these salts contributes to the good effect, or whether they act by the bases alone.

Nitrate of ammonia crystallises in prisms like those of nitrate of potash. It is used in the preparation of the protoxide of nitrogen or laughing gas. Formula,  $\text{NH}_4\text{O}, \text{NO}_5$ , or  $\text{NH}_4, \text{NO}_6$ .

Nitrate of baryta crystallises in octohedrons, which are anhydrous. It is much used as a test, and when ignited yields pure baryta. Formula,  $\text{BaO}, \text{NO}_5$ , or  $\text{Ba}, \text{NO}_6$ .

Nitrate of strontia forms anhydrous crystals, isomorphous with the preceding salt; but it also occurs in large prismatic crystals, containing 5 eqs. of water. It is used in the manufacture of red fire.

Nitrate of lime and nitrate of magnesia crystallise with difficulty, and are extremely deliquescent.

Nitrate of copper forms deep-blue crystals, the formula of which is  $\text{CuO}, \text{NO}_5 + 3\text{HO}$ , or  $\text{Cu}, \text{NO}_6 + 3\text{HO}$ . There is also

subnitrate, the formula of which is  $\text{HO},\text{NO}_3 + 3\text{CuO}$  : the former salt may be viewed as nitrate of copper with 3 eqs. of constitutional water, the latter as nitrate of water with 3 eqs. of constitutional oxide of copper. When either is ignited, it leaves pure oxide of copper, well adapted for organic analysis.

Nitrate of lead crystallises in octohedrons, and is isomorphous with the nitrates of baryta and strontia. Formula,  $\text{PbO},\text{NO}_3$ , or  $\text{Pb}_2\text{NO}_6$ .

Nitrate of mercury is of uncertain composition : there seem to be nitrates both of protoxide and peroxide, but both have a great tendency to form sub-salts, especially in contact with water. When heated, the acid is driven off, and peroxide of mercury is left.

Nitrate of silver, or lunar caustic, is very much used as an escharotic. It is made by dissolving pure silver, or the oxide formed from the chloride (see p. 314) in nitric acid and evaporating, when crystals are deposited, which are fine tables, anhydrous, and fusible at  $426^\circ$ , when they may be run into a mould so as to yield the sticks of caustic. Formula,  $\text{AgO},\text{NO}_3$ , or  $\text{Ag}_2\text{NO}_6$ . It is the chief ingredient of indelible ink. Like all the other compounds of silver, it is blackened by light, especially when in contact with organic matter. It is much used as a test for chlorine.

#### CHLORATES.

The chlorates are, both in formula and properties, very analogous to the nitrates. They deflagrate violently with combustible matter, and are easily distinguished from nitrates by leaving chlorides when ignited. Their general formula is,  $\text{MO},\text{ClO}_3$ , or  $\text{M}_2\text{ClO}_6$ .

The only important chlorate is chlorate of potash, the theory of the production of which has been already explained. It forms tabular crystals, of a pearly lustre. It is chiefly used as a convenient source of very pure oxygen gas, and as an oxidising agent. Its formula is  $\text{KO},\text{ClO}_3$ , or  $\text{K}_2\text{ClO}_6$ .

The perchlorate of potash,  $\text{KO},\text{ClO}_4$ , or  $\text{K}_2\text{ClO}_8$ , is the only perchlorate of interest. It is so sparingly soluble that perchloric acid may be used as a test for potash. It deflagrates with combustible matter, although not so powerfully as the chlorate.

#### HYPOCHLORITES.

These salts do not, in themselves, possess much importance, but are interesting as forming part of the bleaching compounds

of lime and soda, so much used in the arts. These bleaching compounds, as formerly explained, are formed when chlorine acts on an alkali or alkaline earth, and may be viewed either as composed of a hypochlorite and a chloride, or as oxychlorides of the metal. According to the former view, which is the more probable, bleaching-powder is  $(\text{CaO}, \text{ClO}) + \text{CaCl}$ . When acted on by an acid, the whole of its chlorine is set free, and hence, its enormous bleaching power when an acid is used; hence, also, its want of bleaching power, unless acid is added. The action of sulphuric acid is as follows:  $(\text{CaO}, \text{ClO} + \text{CaCl}) + 2\text{SO}_3 = 2(\text{CaO}, \text{SO}_3) + \text{Cl}_2$ . According to the latter view, bleaching powder is  $\text{CaOCl}$ , an oxychloride, and the action of sulphuric acid is  $\text{CaOCl} + \text{SO}_3 = \text{CaO}, \text{SO}_3 + \text{Cl}$ .

Chloride of soda, a perfectly analogous compound, is either  $\text{NaO}, \text{ClO} + \text{NaCl}$ , or  $\text{NaOCl}$ ; and its action with sulphuric acid is explained exactly as above.

#### IODATES.

These salts are, in general, analogous to the chlorates, but are of little practical importance. The general formula for an iodate is,  $\text{MO}, \text{IO}_5$ , or  $\text{M}, \text{IO}_6$ . When heated to redness, oxygen is given off, and an iodide remains.

The bromates are quite analogous to the chlorates. General formula,  $\text{MO}, \text{BrO}_5$ , or  $\text{M}, \text{BrO}_6$ .

#### PHOSPHATES.

There are three distinct modifications of phosphoric acid, each of which forms its own salts. Indeed were it not that these acids, under certain circumstances, may be made to pass into each other, we should never think of describing them otherwise than as totally distinct acids. The three acids are, monobasic, bibasic, and tribasic phosphoric acids.

The so-called anhydrous phosphoric acid, formed by burning phosphorus in dry air or oxygen, is not, strictly speaking, an acid, and does not acquire acid properties till it has taken up the elements of at least 1 eq. of water, when it becomes monobasic phosphoric acid.

According to the usual view, the three acids are  $\text{PO}_5, \text{HO}$ ;  $\text{PO}_5, 2\text{HO}$ ; and  $\text{PO}_5, 3\text{HO}$ , thus containing, all of them, anhydrous acid united with different proportions of water. Now this is quite conceivable, and we actually possess three distinct hydrates of sulphuric acid,  $\text{SO}_3, \text{HO}$ ;  $\text{SO}_3, 2\text{HO}$ ; and  $\text{SO}_3, 3\text{HO}$ . But we find, further, that the acid,  $\text{PO}_5, \text{HO}$ , requires but 1 eq. of base, to form a neutral salt, while the acid  $\text{PO}_5, 2\text{HO}$  requires

2 eqs., and the acid  $\text{PO}_5, 3\text{HO}$ , 3 eqs. of base to form neutral salts. In the case of sulphuric acid the same phenomenon does not occur, for all the hydrates are neutralised by 1 eq. of base, yielding the same salt, and not, as the phosphoric acids do, different salts. What is the cause of this difference? It is not enough to say that the dry acid,  $\text{PO}_5$ , being in the monobasic form combined with 1 eq. of water, has a tendency to take 1 eq. of base, and so on; for this is merely re-stating the fact in other words; and besides, no such tendency is observed in sulphuric and in many other acids.

It appears to me that the only satisfactory answer to the question is the following. The three acids are all distinct acids, and none of them contain anhydrous phosphoric acid. They are all hydrogen acids; and their respective formulæ are  $\text{PO}_6, \text{H}$ ;  $\text{PO}_7, \text{H}_2$ ; and  $\text{PO}_8, \text{H}_3$ . Now as every hydrogen acid forms a neutral salt by the substitution of a metal for the hydrogen, these acids, if they exist, must require respectively, 1, 2, and 3 eqs. of base to neutralise them, and must, of course, produce totally distinct salts: according to the equations,  $\text{PO}_6, \text{H} + \text{MO} = \text{PO}_6, \text{M} + \text{HO}$ ;  $\text{PO}_7, \text{H}_2 + 2\text{MO} = \text{PO}_7, \text{M}_2 + 2\text{HO}$ ; and  $\text{PO}_8, \text{H}_3 + 3\text{MO} = \text{PO}_8, \text{M}_3 + 3\text{HO}$ .

#### MONOBASIC PHOSPHATES.

According to the above views, therefore, the general formula for a monobasic phosphate is  $\text{PO}_6, \text{M}$ , or  $\text{PO}_5, \text{MO}$ . Monobasic phosphate of soda,  $\text{PO}_6, \text{Na}$ , or  $\text{PO}_5, \text{NaO}$ , is obtained by heating the acid tribasic phosphate of soda to redness, when it loses 2 eqs. of water, and monobasic phosphate is left. It is soluble but not crystallisable, and gives, with chloride of barium, a bulky precipitate, which is  $\text{PO}_6, \text{Ba}$ , or  $\text{PO}_5, \text{BaO}$ ; and with nitrate of silver, a flaky white precipitate, which is  $\text{PO}_6, \text{Ag}$ , or  $\text{PO}_5, \text{AgO}$ .

#### BIBASIC PHOSPHATES.

Of these there are two series, as one of the 2 eqs. of base may be basic water, or both may be fixed base. The general formulæ for the two series are  $\text{PO}_7, \text{M}_2$ , or  $\text{PO}_5, 2\text{MO}$ ; and  $\text{PO}_7 \begin{Bmatrix} \text{H} \\ \text{M} \end{Bmatrix}$  or  $\text{PO}_5 \begin{Bmatrix} \text{HO} \\ \text{MO} \end{Bmatrix}$ . Bibasic phosphate of soda,  $\text{PO}_7, \text{Na}_2$ , or  $\text{PO}_5, 2\text{NaO}$ , is obtained by exposing to a red heat common tribasic phosphate of soda, which loses 1 eq. of water, and is converted into the new salt. It is soluble and crystallisable, and gives, with nitrate of silver, a granular white precipi-

pitate, which is  $\text{PO}_7, \text{Ag}_2$ , or  $\text{PO}_5, 2\text{AgO}$ . When the acid tribasic phosphate of soda is heated to  $400^\circ$ , it loses 1 eq. of water, and leaves the acid bibasic phosphate,  $\text{PO}_7 \left\{ \begin{smallmatrix} \text{H} \\ \text{Na} \end{smallmatrix} \right.$  or  $\text{PO}_5 \left\{ \begin{smallmatrix} \text{HO} \\ \text{NaO} \end{smallmatrix} \right.$

## TRIBASIC PHOSPHATES.

Of these, which are the most usual phosphates, there are three series, the general formulæ for which are as follows ;  $\text{PO}_8, \text{M}_3$ , or  $\text{PO}_5, 3\text{MO} : \text{PO}_8 \left\{ \begin{smallmatrix} \text{H} \\ \text{M}_2 \end{smallmatrix} \right.$  or  $\text{PO}_5 \left\{ \begin{smallmatrix} \text{HO} \\ 2\text{MO} \end{smallmatrix} \right. : \text{and } \text{PO}_8 \left\{ \begin{smallmatrix} \text{H}_2 \\ \text{M} \end{smallmatrix} \right.$  or  $\text{PO}_5 \left\{ \begin{smallmatrix} 2\text{HO} \\ \text{MO} \end{smallmatrix} \right.$

Common phosphate of soda belongs to the second series : it is  $\text{PO}_8 \left\{ \begin{smallmatrix} \text{H} \\ \text{Na}_2 \end{smallmatrix} \right.$  or  $\text{PO}_5 \left\{ \begin{smallmatrix} \text{HO} \\ 2\text{NaO} \end{smallmatrix} \right.$  when dry, to which, in the crystals, are added 24 eqs. of water of crystallisation. By the addition of caustic soda, it is converted into  $\text{PO}_8, \text{Na}_3$ , or  $\text{PO}_5, 3\text{NaO}$  ; and by the addition of phosphoric acid, until it ceases to precipitate chloride of barium, it is converted into the acid tribasic salt,  $\text{PO}_8 \left\{ \begin{smallmatrix} \text{H}_2 \\ \text{Na} \end{smallmatrix} \right.$  or  $\text{PO}_5 \left\{ \begin{smallmatrix} 2\text{HO} \\ \text{NaO} \end{smallmatrix} \right.$ . With nitrate of silver, either of these three salts yields a lemon-yellow precipitate, which is tribasic phosphate of silver,  $\text{PO}_8, \text{Ag}_3$ , or  $\text{PO}_5, 3\text{AgO}$ .

Microcosmic salt, much used as a blow-pipe re-agent, is a tribasic phosphate,  $\text{PO}_8 \left\{ \begin{smallmatrix} \text{H} \\ \text{Na} \end{smallmatrix} \right. + 8 \text{ aq.}$  or  $\text{PO}_5 \left\{ \begin{smallmatrix} \text{HO} \\ \text{NaO} \end{smallmatrix} \right. + 8 \text{ aq.}$   $\text{NH}_4$  here represents ammonium.

Bone phosphate of lime is  $\text{PO}_5, 3\text{CaO}$ , with some carbonate of lime and fluoride of calcium.

The double phosphate of ammonia and magnesia, which occurs in some urinary calculi, and is also found in the husk of grain and other vegetable products, is  $\text{PO}_5, 2\text{MgO}, \text{NH}_4\text{O}$ . - 12 aq. This salt always separates as a sparingly soluble, or insoluble granular precipitate, when phosphoric acid, ammonia, and magnesia meet in neutral or alkaline solutions, and therefore its formation may be made a test, either of the presence of phosphoric acid, or that of magnesia.

## ARSENIATES.

The salts of arsenic acid are extremely analogous to those of tribasic phosphoric acid ; indeed, they are so similar, in form,



colour, solubility, &c., that to distinguish the arseniate of a base from the corresponding tribasic phosphate, we must ascertain the presence of arsenic. The only case in which a well-marked difference in external properties exists, is in the case of the arseniate of silver, which, instead of being yellow, like the corresponding tribasic phosphate, is of a dark, brick-red colour. The arseniates are tribasic, and their general formulæ are,  $\text{AsO}_3, \text{M}_3$ ; or  $\text{AsO}_3, 3\text{MO}$  :  $\text{AsO}_3 \left\{ \begin{array}{l} \text{H} \\ \text{M}_2 \end{array} \right.$  or  $\text{AsO}_3 \left\{ \begin{array}{l} \text{HO} \\ 2\text{MO} \end{array} \right.$  and  $\text{AsO}_3 \left\{ \begin{array}{l} \text{H}_2 \\ \text{M} \end{array} \right.$  or  $\text{AsO}_3 \left\{ \begin{array}{l} 2\text{HO} \\ \text{MO} \end{array} \right.$ . Several arseniates are found native.

## CHROMATES.

These salts are yellow, orange, or red, the latter colour predominating when the acid is in excess, except in the case of dichromate of lead, which is red. The soluble chromates are recognised by their colour, which is changed to green when alcohol and hydrochloric acid are added, and the mixture is boiled. The general formula for neutral chromates is  $\text{MO}, \text{CrO}_3$ ; and for bichromates,  $\text{MO}, 2\text{CrO}_3$ .

Neutral chromate of potash,  $\text{KO}, \text{CrO}_3$ , forms beautiful yellow crystals, isomorphous with sulphate of potash. It is formed by neutralising the bichromate with potash.

Bichromate of potash,  $\text{KO}, 2\text{CrO}_3$ , is much used in calico-printing, and is obtained by fusing chrome iron ore with nitre. The ore contains sesquioxide of chromium,  $\text{Cr}_2\text{O}_3$ , which is oxidised by the nitre into chromic acid,  $\text{Cr}_2\text{O}_6 = 2\text{CrO}_3$ , and this combines with the potash of the nitre to form neutral chromate. This is dissolved and filtered, and the warm solution acidulated with acetic acid, which takes half the potash, and, on cooling, the bichromate is deposited in beautiful red crystals.

Both these salts, especially the bichromate, have a very deleterious action on the system, when their solutions are brought much in contact with the skin, causing sores, which are very painful and difficult to heal. Paper impregnated with these salts, and dried, forms excellent tinder. The solutions have very powerful antiseptic properties.

Dichromate of lead,  $2\text{PbO} + \text{CrO}_3$ , is found native, as the red-lead ore, forming beautiful red crystals. It may also be formed by fusing the neutral chromate of lead with nitrate of potash, or by boiling carbonate of lead with chromate of potash; and is much used as a paint.

Chromate of lead,  $\text{PbO}, \text{CrO}_3$ , is an insoluble powder, of a very fine yellow colour, much used in painting, under the name

of chrome yellow. It is formed by the action of soluble salts of lead on chromate, or bichromate of potash.

Chromate of silver,  $\text{AgO}, \text{CrO}_3$ , forms dark-green crystals, which are red by transmitted light, and yield a deep-red powder. When precipitated, the salt is of a rich dark-red.

Bichromate of silver forms crimson-red tabular crystals,  $\text{AgO}, 2\text{CrO}_3$ . Chromate of mercury,  $\text{AgO}, \text{CrO}_3$ , is a light-red powder, which, when ignited, leaves sesquioxide of chromium of a very fine green colour.

#### BORATES.

The only important borate is borax, which is a biborate of soda,  $\text{NaO}, 2\text{BO}_3 + 10 \text{ aq.}$  It is found native, but very impure, in Thibet, and is purified in Europe. It is also now formed by adding soda to the native boracic acid obtained from hot springs in Tuscany. Boracic acid is so feeble an acid that even the 2 eqs. of it in borax do not fully neutralise the soda, so that borax is an alkaline salt. The borate of soda, with 1 eq. of acid,  $\text{NaO}, \text{BO}_3 + 8 \text{ aq.}$ , is a strongly alkaline salt. The mineral boracite is a compound of borate and biborate of magnesia,  $2(\text{MgO}, \text{BC}_3) + (\text{MgO}, 2\text{BO}_3)$ .

Borax is much used as a flux, on account of its ready fusibility and its high solvent power, at a red-heat.

#### SILICATES.

Silicic acid is so weak an acid, that it combines in almost all proportions with bases. When potash or soda in excess are fused with silicic acid, glassy silicates are formed which are soluble in water. The neutral silicate of soda crystallises, and the crystals are  $\text{NaO}, \text{SiO}_3 + 9 \text{ aq.}$  A peculiar silicate, formed by heating 8 parts of carbonate of soda, or 10 of carbonate of potash, with 15 parts of silica and 1 of charcoal, is called Fuchs's soluble glass. It dissolves in 4 or 5 parts of hot water, but not in cold water. The solution is used to render wood and cloth incombustible.

All the silicates of the other metals are insoluble, and from this cause they are abundant in the mineral kingdom, as water cannot carry them away, as it does soluble salts.

The alkaline silicates, with excess of acid, are also insoluble, and from the peculiar tenacity they possess in the half-fused condition, a property which they communicate to earthy and metallic silicates, while at the same time, being themselves glassy and amorphous, they prevent the crystallisation of other

silicates, they constitute the basis of glass, and are of great practical importance.

Glass varies much in composition, but is fundamentally a mixture of silicate of potash or soda, with silicates of lime, baryta, magnesia, alumina, and lead. It is coloured by iron, manganese, copper, cobalt, uranium or gold. An excess of silica is generally present.

Bohemian glass consists chiefly of the silicates of potash and lime; as does also the hard infusible glass used in the laboratory, which latter approaches to the formula,  $\text{KO}, 3\text{SiO}_3 + \text{CaO}, 3\text{SiO}_3$ , in which part of the potash is sometimes replaced by soda, and part of the lime by magnesia. The more fusible kind used for the beautiful Bohemian ware, contains also silicate of alumina, approaching to  $\text{KO}, \text{SiO}_3 + 2(\text{CaO}, \text{SiO}_3) + (\text{Al}_2\text{O}_3, 3\text{SiO}_3)$ .

Crown glass, used for lenses, is nearly  $\text{KO}, \text{SiO}_2 + \text{CaO}, \text{SiO}_2$ . Plate-glass and window-glass contain silicates of soda and lime, and are more fusible than potash glass; plate-glass requiring to be cast.

Window-glass, and all other kinds which are blown, are allowed to cool after being fully melted, and when half-solid, possess the requisite ductility and tenacity.

Bottle-glass is a less pure kind, containing silicates of alumina, lime, iron, magnesia, and soda or potash. A sample analysed by Dumas, approached to the formula,  $6[(\text{CaK})\text{O}, \text{SiO}_3] + (\text{AlFe})_2\text{O}_3, 3\text{SiO}_3$ . The two metals within brackets are such as replace each other in variable proportions.

When glass, especially bottle-glass, is very slowly cooled, it undergoes a molecular change, like that which occurs in amorphous sugar (barley-sugar) when kept; it becomes crystalline, opaque, and hard, and is then called Reaumur's porcelain.

Flint-glass, or crystal, is a very fusible glass, which contains silicate of lead along with silicate of potash. It is nearly  $\text{KO}, 3\text{SiO}_3 + \text{PbO}, 3\text{SiO}_3$ , or when richer in lead, nearly  $2(\text{KO}, 3\text{SiO}_3) + 3(\text{PbO}, 3\text{SiO}_3)$ . It contains  $\frac{1}{3}$  of its weight, or more, of oxide of lead, and has a Sp. G. varying from 3.28 to 4.75.

Faraday's optical glass consists of silicate and borate of lead, and has a Sp. G. of 5.44. A similar glass, with oxide of zinc, instead of oxide of lead, has been proposed for optical purposes.

The glass used to imitate gems contains half its weight of oxide of lead, and has a very high refracting power. It is coloured, as all glass may be, amethyst by oxide of manganese, green by protoxide of copper or sesquioxide of chromium, blue by oxide of cobalt, ruby-red by suboxide of copper; and a still finer ruby-red by gold; yellow with green reflex by peroxide of

uranium, other yellows by oxide of silver or oxide of antimony, and black by a mixture of oxides of manganese and cobalt. The various greenish tints of bottle-glass are due to protoxide of iron, and when the presence of a little of this oxide gives a green tint to what ought to be colourless glass, a little oxide of manganese peroxidises the iron and destroys the colour. This plan is usually followed because even the purest native materials contain traces of iron.

Enamel is opaque glass ; rendered so by peroxide of tin or stannic acid, by phosphate of lime, oxide of antimony, or arsenious acid. It is coloured in the same way as glass.

Though insoluble in water under ordinary pressure, glass is rapidly dissolved by boiling water under high pressures.

The natural silicates are very numerous. Chrysolite or olivine, talc, steatite, meerschaum, and serpentine, are all silicates of magnesia. Augite or pyroxene is a silicate of lime and magnesia, partly replaced by iron and manganese. Hornblende or amphibole is a silicate and aluminate of lime, magnesia, and iron. For the formulæ, see works on Mineralogy.

Felspar is a double silicate of alumina and potash,  $\text{KO}$ ,  $\text{SiO}_3 + \text{Al}_2\text{O}_3$ ,  $3\text{SiO}_3$ . Soda replaces the potash, forming albite or soda felspar, and lithia does so, forming petalite or lithia felspar. Clay is fundamentally  $2\text{Al}_2\text{O}_3 + 3\text{SiO}_3 + 4\text{ac}$ . It is derived from the disintegration of felspar. Labradorite is a lime felspar. Mica is also a double silicate of alumina (and iron) with potash (protoxide of iron and magnesia), with the addition of a small proportion of a fluoride. Garnet and idocrase are basic double silicates of lime and alumina. Chlorite is a double silicate of lime and magnesia. Beryl is a silicate of alumina and glucina ; chryso-beryl an aluminate of glucina.

Zeolites are hydrated double silicates, chiefly of alumina and lime. They contain silica in a soluble form, and are converted into a jelly by strong hydrochloric acid. Stilbite and prehnite contain the same ingredients ; analcime is a silicate of alumina and soda.

Porcelain, being made from clay, is, like it, a silicate of alumina, with small quantities of other oxides.

#### CARBONATES.

These salts are recognised by their being decomposed with effervescence, the gas disengaged having no offensive smell, when acted on by acids. All the soluble carbonates, even those containing 2 eqs. of acid to one of base, are alkaline, so that

carbonic acid is a very feeble acid. Like silicic acid, it combines, at least with some bases, in numerous proportions.

Carbonate of potash,  $\text{KO}, \text{CO}_2$ , is anhydrous, deliquescent, not crystallisable, insoluble in alcohol. It is obtained pure by igniting cream of tartar, and lixiviating the residue. In an impure state it constitutes pearlash and potashes, which are, as the name implies, the ashes of plants. Carbonate of potash is much used as a flux in mineral analysis, and for the preparation of caustic potash, and other salts of potash; also in the manufacture of soap, and of glass.

Bicarbonate of potash,  $\text{KO}, 2\text{CO}_2 + 2 \text{ aq.}$ , is obtained by exposing a strong solution of the carbonate to a current of carbonic acid, or to the atmosphere of a fermenting vat, when the bicarbonate is deposited in crystals. The purest carbonate is obtained by igniting these crystals.

Carbonate of soda,  $\text{NaO}, \text{CO}_2 + 10 \text{ aq.}$ , forms very large rhomboidal crystals, which effloresce in the air. It was formerly extracted from kelp or barilla, which is the ashes of marine plants; but is now made from sea-salt, far more cheaply, and in a state of perfect purity. The salt,  $\text{NaCl}$ , is first converted into sulphate of soda,  $\text{NaO}, \text{SO}_3$ , by being heated with oil of vitriol. The sulphate of soda is now mixed with sawdust and lime, and heated in a reverberatory furnace. By this means the sulphuric acid is decomposed, its sulphur partly uniting with calcium, and partly escaping as sulphurous acid, while the carbonic acid which is formed unites with soda. The carbonate is purified by crystallisation, but generally retains a trace of sulphuric acid.

Carbonate of soda is very much used in the making of soap and glass, being both much cheaper and much purer than ordinary potash. It is also much employed by washerwomen to render hard water soft, and in general to assist in washing, as it is powerfully detergent.

Bicarbonate of soda,  $\text{NaO}, 2\text{CO}_2 + \text{aq.}$ , forms a white powder which is alkaline, and is much used in medicine as a mild antacid, and as one of the ingredients in effervescing or Seidlitz powders.

The common commercial and medicinal carbonate of ammonia is a sesquicarbonate,  $2\text{NH}_3 + 2\text{HO} + 3\text{CO}_2$ . It is formed by heating a mixture of 2 parts of sal-ammoniac and 3 of dried chalk, and sublimes as a hard crystalline volatile mass, having a strong smell of ammonia. When exposed to air, it loses ammonia, and falls to a powder of bicarbonate,  $\text{NH}_4\text{O}, \text{CO}_2 + \text{HO}, \text{CO}_2$ . There are many other carbonates of ammonia, all strongly alkaline in character.

Carbonate of baryta occurs native, as witherite. It forms, when artificially prepared, a heavy white powder, soluble in diluted hydrochloric and nitric acids, insoluble in water. It is very poisonous. Formula,  $\text{BaO}, \text{CO}_2$ .

Carbonate of strontia resembles the preceding. It occurs native, as strontianite, in radiated crystalline masses of an apple-green colour. It is not poisonous. Formula,  $\text{SrO}, \text{CO}_2$ .

Carbonate of lime occurs native, as marble, limestone, chalk, arragonite, and calcareous spar. It also forms the chief part of shells, and is often found in springs, dissolved by an excess of carbonic acid. When such water, which is very hard, is boiled, the excess of carbonic acid escapes, the carbonate of lime is deposited, and the water becomes, *pro tanto*, softer. Or, the same effect may be produced by adding just as much lime-water as will neutralise the bicarbonate of lime, when the whole is precipitated as neutral carbonate,  $\text{CaO}, 2\text{CO}_2 + \text{CaO} = 2(\text{CaO}, \text{CO}_2)$ .

When carbonate of lime is ignited in the open fire, it loses all its carbonic acid and becomes quicklime. The uses of this substance are well known. Formula of carbonate of lime,  $\text{CaO}, \text{CO}_2$ .

Carbonate of magnesia,  $\text{MgO}, \text{CO}_2$ , occurs as a rock in the East Indies. When a solution of bicarbonate is exposed to the air, crystals are deposited, which are  $\text{MgO}, \text{CO}_2 + 3 \text{ aq.}$  Other crystals have been obtained, which were  $\text{MgO}, \text{CO}_2 + 5 \text{ aq.}$  When carbonate of potash is added to a solution of sulphate of magnesia, a precipitate falls, which contains  $4\text{MgO} + 3\text{CO}_2 + 4 \text{ aq.}$

Carbonate of protoxide of iron is formed when an alkaline carbonate is added to a solution of protosulphate of iron. It falls as a dirty white bulky precipitate, which rapidly becomes green, and then brown, losing carbonic acid, and attracting oxygen, till it passes into hydrated peroxide of iron. It may be preserved as protocarbonate by mixing the fresh precipitate while still moist with sugar, and drying it in the water bath. In this state it is the *carbonas ferri saccharatus*, and is a very active remedy. It occurs in chalybeate waters, dissolved by excess of carbonic acid. Formula,  $\text{FeO}, \text{CO}_2 + \text{aq.}$

There are two native carbonates of copper: the dicarbonate,  $2\text{CuO} + \text{CO}_2 + \text{aq.}$ , in the beautiful green mineral called malachite; and the carbonate, hydrated, in the fine blue copper ore,  $\text{CuO}, \text{HO} + 2(\text{CuO}, \text{CO}_2)$ .

Carbonate of lead,  $\text{PbO}, \text{CO}_2$ , occurs native as white lead spar. Prepared artificially, it is ceruse, or white lead, much used as a white pigment. It is formed by the slow action of air, moi-

ture, and the vapour of acetic acid on thin sheets of lead, by which the metal is oxidised and carbonated. It is the most poisonous of all the compounds of lead, and is apt to be formed when pure water (as rain water) is kept in leaden cisterns or conveyed in leaden pipes. It is not formed, however, when the water contains even a small proportion of saline matter, especially sulphates. These appear to protect the metal, and render the use of it safe.

## SULPHUR SALTS.

Berzelius has shown that sulphurets unite together, and produce, what he calls sulphur salts. The sulphurets of potassium, sodium, and the strongly-basic metals in general, act the part of bases ; and the sulphurets of arsenic, antimony, molybdenum, &c., assume the function of acids. Thus tersulphuret of arsenic combines with sulphuret of potassium, forming the arsenio-sulphuret of potassium,  $KS + AsS_3$ , which corresponds to the arsenite of potash,  $KO + AsO_3$  ; and as a general rule, the sulphur salts correspond to oxygen salts, and may of course be represented in two ways ; as, if we make the arsenite of potash  $K + AsO_4$ , the sulphur salt will be  $K + AsS_4$ . The sulphurets of hydrogen and carbon are sulphur acids. The sulphur salts, as yet, are not of much practical interest, although the tendency to form them is applied to useful purposes in analysis.

Selenium and Tellurium form similar compounds.





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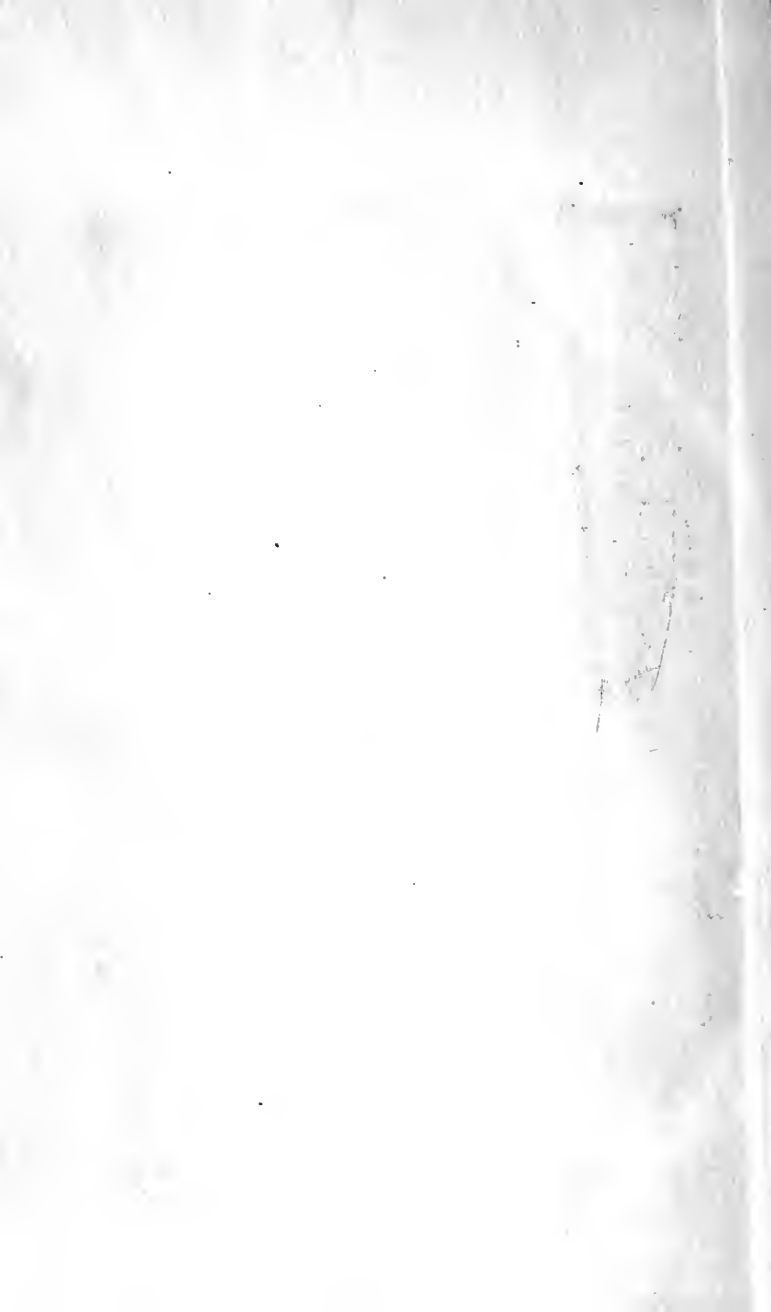
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